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Office of Naval Research
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The conference "Molecular Quantum Mechanics: Analytic Gradients and Beyond" was held May 29-June 3, 2007 in Budapest, Hungary. Enclosed are the conference poster and program/abstract book. At the top of page II of the program/abstract book, the support of the Office of Naval Research is acknowledged. A book related to the conference was published by Taylor & Francis (ISBN 0-415-34264-3), with the PI as one of three authors. The conference proceedings were published in the journal of *Molecular Physics*, Volume 105, pages 2439-2926.

The US participants in the conference included fifteen plenary lectures and seventeen session chairs. The ONR funds were used to pay the registration fees of all of these U. S. citizen scientists. Dr. Peter Schmidt represented the ONR at the meeting.

All reports coming to the organizers were in agreement that this was one of the best theoretical chemistry conferences on record.

$\tilde{\mathbf{g}}_n = \mathbf{g}(\mathbf{X}_n) + \sum_{i=1}^{n-1} c_i (\mathbf{g}_i - \mathbf{g}_{n-1})$

Program and Abstracts

$$c_i = \frac{\sum_j B_{ij}^{-1}}{\sum_{jk} B_{jk}^{-1}}$$

$$H_0 = P_0 FP_0 + P_S FP_S^T + P_D FP_D^T$$

Molecular Quantum Mechanics: Analytic Gradients and Beyond

A Conference in Honor of Peter Pulay

May 29 – June 3, 2007
Margitsziget, Budapest, Hungary

20090814023

Program and Abstracts

Molecular Quantum Mechanics – Analytic Gradients and Beyond A Conference in Honor of Peter Pulay

May 29 – June 3, 2007

Margitsziget, Budapest, Hungary

Yanming Xie

Organizers:

Attila G. Császár, Géza Fogarasi, Henry F. Schaefer III, and Péter G. Szalay

AQ F09-11-03222

The organizers are appreciative of the generous support of the IBM Corporation (Dr. James Coffin), the U.S. Office of Naval Research (Dr. Peter Schmidt), Gedeon Richter Ltd., and Taylor&Francis for the conference.

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General Information

Conference Venue

The Conference is held in Budapest, on Margaret Island at the Danubius Health Spa Resort Hotel (1138 Budapest, Margitsziget). Sessions will take place in the Star Auditorium, poster sessions will take place in the Jasmine Room of the hotel.

The Conference site can be reached easily by public transportation. Margaret Island is closed for cars, vehicles must park in the parking area belonging to the Conference venue. Only public transportation is allowed on the island - bus Nr. 26 runs along the island between Western (Nyugati) Railway station and Arpad Bridge.

Registration Desk and Hours

The Registration Desk, where advance and on-site registrants may pick up their conference material is operating at the lobby area of the Danubius Health Spa Resort Hotel. The representatives of Chemol Travel will be at your service at the registration. They are in charge of the registration, hotel bookings, social events, and optional excursions. Tickets for social events and optional tours can be obtained at the registration desk. Travel agency service will also be provided as follows:

Tuesday, May 29 th	14:00 - 20:00
Wednesday, May 30 th	08:00 - 19:00
Thursday, May 31 st	08:30 - 19:00
Friday, June 1 st	08:30 - 19:00
Saturday, June 2 nd	08:30 - 19:00
Sunday, June 3 rd	08:30 - 14:00

Conference Badge

Participants will receive a badge upon registration. Admission to the Conference & Poster Session area and/or to the social activities is possible only with a valid badge. Badges must be worn throughout the conference and at social events.

Certificate of Attendance

A Certificate of Attendance can be requested at the Registration desk.

Technical Equipments & Instruction for oral presentations

"Power Point" on a PC, running Windows XP with Office XP, is available in the Star Auditorium. You may connect your own computer to the projector if you prefer and arranged that in advance.

Speakers are requested to test and hand over their CD ROM or pen drive to the technician on the day before their presentation, if the presentation is in the morning session, or minimum 3 hours before the session in case of an afternoon session. Please consult with the technician in the lecture room before your session.

Optimal conditions of presentation files:

Presentation file: Microsoft Powerpoint or PDF (if you want to use other software, please bring it to the Conference). If you use animations, please embed them. If it is a special animation, please send the codec to the Conference Secretariat and bring all the files on a CD/pen drive to the Conference. If you have a Macintosh computer, it can be plugged in having a conventional, 15-pin socket. If your computer does not have this connection, please bring an appropriate converter with you.

Instructions for poster presentations

Posters will be on display for one day only. The poster boards are 1 meter (40 inches) wide and 2 meter (80 inches) tall. The suggested size of the poster is 90 cm x 130 cm (width x height).

Poster presenters are asked to mount their posters early in the morning, preferably between 08:30 and 9:30 am. Poster discussion will be as given in the program.

Double adhesives and pins will be available at the Poster Desk (Jasmine Room).

Language

The official language of the Conference is English.

Liability

The organizers cannot accept liability for any personal accidents, loss of belongings or damage to private property of participants and accompanying persons that may occur during the Conference.

Meals

Coffee/Tea during the coffee breaks will be available for the registered participants in the Ground floor foyer in front of Jasmine Room.

Buffet lunch is also available for the registered participants in the Platan Restaurant at Danubius Health Spa Resort Hotel.

Currency, Exchange, Credit Cards

The official currency in Hungary is Hungarian Forint (HUF). Exchange facilities are offered to participants at the airport, in hotels, at the exchange desk of the banks or at the registration desk at a daily indicated rate.

American Express, Visa, Eurocard, Master Card are accepted at the registration desk, in hotels, first class restaurants and city stores, but you should ask or look for the logo before ordering a service.

Most banks are open from Monday to Friday between 08:00 and 16:00hrs. On Saturdays and Sundays banks are closed. Most hotels do not accept travellers cheques for payment of their accounts or for cash. You can cash travellers cheques at banks.

Coat check/ luggage storage

You will find a coat check /luggage storage room in the hotel lobby on the conference level, operating between 08:30 – 18:30.

Please note that we cannot take responsibility for valuable belongings such as passports, cash, etc. Please remove these from your coats / luggage before storage.

Electricity Supply

The voltage in Hungary is 220 Volts. Round European-style two-pin plugs are used. Appliances designed to operate on 110/120V need a voltage converter and a plug adapter for two-prong, round-prong plugs with side grounding contacts.

Local Transportation in Budapest

Public transport in the city is well organized. Trams, buses and metro operate without conductors. Tickets must be purchased in advance at tobacco shops or metro stations. Weekly passes allowing free travel on all means of transportation within the city borders can be bought at all main metro stations.

Taxis

We suggest that you use only taxis equipped with a taximeter, such as Tele5, Fõtaxi, City Taxi or Buda Taxi. Beware of private cabs, especially those without a taximeter.

Telephones

Most public telephones in Budapest are on a digital network. Blue pay-phones take 10, 20, 50 and 100 forint coins. There are more silver card phones. Phone-cards can be bought at hotels, post offices, petrol and railway stations as well as at newsstands. Emergencies (Ambulance, Police and Fire Department) can be called without coins. Phone numbers in case of emergency:

General emergency: 112, Fire department: 105, Ambulance: 104, Police: 107

Tipping

It is customary to give a tip of 10% over the amount of the bill at restaurants, unless it is included in the bill, and when riding a taxi.

Note for drivers

Drivers should be aware that there is a zero tolerance of blood alcohol level while driving in Hungary.

Weather

As Hungary has continental climate, the beginning of June is also the beginning of the summer. The average temperature is 18-25°C during the day and 14-18°C at night. The humidity is usually low, but rainy days can be expected.

Parking

Limited parking is available in the open-air public parking area in front of the conference venue or at the garage of the hotel (only for hotel guests). Be warned that parking is free only for guests of the two hotels on Margaret Island. All others will need to pay HUF 265 (about EUR 1.10, or USD 1.50) per hour with no possibility for a daily fee. Therefore, all those who are not staying at the Thermal Hotel or Grand Hotel but have a car are encouraged to use public transportation to get to the conference venue.

Shopping hours

The usual shopping hours in Budapest are from 10:00 am to 6:00 pm, in large shopping centers in and around the city until 9 pm.

For further information please contact the Registration Desk.

Smoking

Smoking is NOT permitted inside the Conference building or at the venues for the social functions. Smokers are required to smoke outdoors in the designated area.

Restaurants

For information on restaurants in Budapest, please contact the Registration Desk.

Social Programs

Tuesday, May 29, 19:30 – 21:00

Welcome Reception

Participants of the conference are invited to take part in a standing buffet reception held in Széchenyi Restaurant of Danubius Grand Hotel Margitsziget (approx. 50 metres walk from Danubius Health Spa Resort Hotel).

The Welcome Reception is included in the registration fee and open to all registered participants and accompanying persons.

Wednesday, May 30, 19:00 – 22:00

Hungarian Dinner

Located on Shipyard Island close to the city centre, this Hungarian restaurant offers a nice view of the Danube. It is decorated with rustic-style wooden chairs and tables giving the feel of a traditional Hungarian restaurant. Upon arrival guests are greeted by the master of the house, who welcomes everybody with special fruit brandy and fresh salty scones. An unforgettable evening is guaranteed by gipsy music and authentic folklore show, as well as typical local dishes and a good selection of wines.

Optional, price: 45.- € / person (incl. transfer)

Friday, June 1, 19:30-22:30

Conference Banquet

Join us to experience the most beautiful illuminated sights of Budapest from the blue highway of the capital, the River Danube. An atmospheric boat cruise with seated dinner, music and dance will guarantee superb entertainment for this evening.

Optional, price: 25.- € / person

Tours for Accompanying persons

May 29; June 1, 2 or 3

City tour of Budapest by coach

On this three-hour coach tour you will discover the main attractions of the Hungarian capital. The tour includes a visit to the Heroes' Square with the Millenary Monument, to the St. Stephen Cathedral, to the Opera House and the Parliament to enjoy their spectacular architecture from outside. Continuing on to Buda, you will visit the medieval Castle District, passing by the Fisherman's Bastion and the old Matthias Church, followed by a ride to Gellért Hill, where you will enjoy the beautiful panorama of the city featured on the UNESCO list of World Heritage.

Included in the registration fee for Accompanying persons

May 30

Szentendre Tour

Half-day excursion to one of the most scenic parts of Hungary. The tour includes a visit to Szentendre, the artists' town with its cobbled-stone squares and picturesque old streets and alleys. After a short guided tour of the town, you'll visit the Kovács Margit Ceramic Museum, a unique place that exhibits the works of a very special Hungarian artist who created her own style by combining modern art forms with the traditions of Hungarian folk art. There will be possibility for shopping in the many handicrafts' and souvenir shops, too, while you'll also taste a typical Hungarian lunch in one of the atmospheric local restaurants of Szentendre.

Included in the registration fee for Accompanying persons

Optional Tours and excursions

We are pleased to offer several exciting optional tours and excursions to all participants of the Conference. Please kindly contact the Registration Desk for further information and tickets.

Scientific Program of the Pulay Conference

May 29 – June 3, 2007

TUESDAY, May 29, 2007			
17:15 – 17:30	Official Opening (Star Auditorium) Henry F. Schaefer III, conference organizer Ferenc Hudecz, Rector of Eötvös University (ELTE) Norbert Kroó, Vice President of the Hungarian Academy of Sciences		
Section: Techniques of MQM (Star Auditorium)			
17:30 – 18:05	O1	William A. Goddard (Pasadena, CA, U.S.A.)	Chair: Emily Carter (Princeton, NJ, U.S.A.) <i>First Principles Approaches to Design of Materials with Applications to Catalysis, Nanoelectronics, Fuel Cells, and Pharma</i>
18:05 – 18:40	O2	Reinhart Ahlrichs (Karlsruhe, Germany)	Chair: Björn O. Roos (Lund, Sweden) <i>Clusters of Boron: Experimental and DFT Treatment of B_{12}-B_{30}</i>
18:40 – 19:15	O3	Debashis Mukherjee (Kolkata, India)	Chair: Péter Surján (Budapest, Hungary) <i>Recent Advances in State-Specific Multi-Reference Coupled Cluster Formalism</i>
19:30 – 21:00	<i>Welcome Reception</i> (Széchenyi Restaurant, Grand Hotel Margitsziget)		

WEDNESDAY, May 30, 2007

Section: Analytic Derivatives (Star Auditorium)			
9:00 – 9:20	H1	Wilfried Meyer (Kaiserslautern, Germany)	Chair: Svein Saebo (Mississippi State, MS, U.S.A.)
<i>Early Developments of Analytic Techniques</i>			
9:20 – 9:55	O4	Mihály Kállay (Budapest, Hungary)	Chair: Svein Saebo (Mississippi State, MS, U.S.A.)
<i>Coupled-Cluster Gradients and Beyond</i>			
9:55 – 10:30	O5	Shigeru Nagase (Okazaki, Japan)	Chair: Krishnan Raghavachari (Bloomington, IN, U.S.A.)
<i>MP2 Energy and Gradient Calculations</i>			
10:30 – 11:00	Coffee break (Ground floor foyer)		
Section: Electron Correlation (Star Auditorium)			
11:00 – 11:35	O6	Peter M. W. Gill (Canberra, Australia)	Chair: Yundong Wu (Hong Kong and Beijing, China)
<i>Electron Correlation: A Hungarian Dance in Three Movements</i>			
11:35 – 12:10	O7	Edward Valeev (Blacksburg, VA, U.S.A.)	Chair: Gregory S. Tschumper (University, MS, U.S.A.)
<i>Efficient Explicitly Correlated R12 Methods Using Gaussian Geminals</i>			
12:10 – 14:00	Lunch break (Platan Restaurant)		
Section: Techniques of MQM (Star Auditorium)			
14:00 – 14:35	O8	Jürg Hutter (Zürich, Switzerland)	Chair: Walter Thiel (Mülheim, Germany)
<i>First-Principles Simulation of Liquids</i>			
14:35 – 15:10	O9	Leo Radom (Sydney, Australia)	Chair: William L. Jorgensen (New Haven, CT, U.S.A.)
<i>Transition-Metal-Free Hydrogenation</i>			
15:10 – 15:45	O10	Julia E. Rice (San Jose, CA, U.S.A.)	Chair: T. Daniel Crawford (Blacksburg, VA, U.S.A.)
<i>Modeling Reactions in Solution: Importance and Complexity</i>			
15:45 – 16:15	Coffee break (Ground floor foyer)		
16:15 – 16:50	O11	Trygve Helgaker (Oslo, Norway)	Chair: Sourav Pal (Pune, India)
<i>The Calculation of Molecular Properties of Large Systems</i>			
16:50 – 17:25	O12	Paul von Rague Schleyer (Athens, GA, U.S.A.)	Chair: Peter R. Schreiner (Giessen, Germany)
<i>Estimating Virtual Quantities: Aromaticity, Strain, Conjugation, Hyperconjugation, and Branching</i>			
17:25 – 18:00	O13	Tom Ziegler (Calgary, Canada)	Chair: Klaus Ruedenberg (Ames, IA, U.S.A.)
<i>Time-Dependent Density Functional Theory As a Practical Tool in the Study of MCD and CD Spectra of Transition Metal Complexes. Implementations and Applications</i>			
18:30 – 21:00	Poster session of conference chairs (Jasmine Room)		

THURSDAY, May 31, 2007

Section: Techniques of MQM (Star Auditorium)			
9:00 – 9:20	H2	Nicholas C. Handy (Cambridge, U.K.) <i>DFT and Plane Waves</i>	Chair: Sue M. Colwell (Cambridge, U.K.)
9:20 – 9:55	O14	Kim Baldridge (Zürich, Switzerland) <i>Structure, Dynamics and Properties of Aromatic Materials Based on Corannulene</i>	Chair: Sue M. Colwell (Cambridge, U.K.)
9:55 – 10:30	O15	Bernard Brooks (Bethesda, U.S.A.) <i>Techniques for Improved Sampling and Free Energies Estimation in Examining Reaction Pathways for Macromolecular Systems</i>	Chair: Weston T. Borden (Denton, TX, U.S.A.)
10:30 – 11:00	<i>Coffee break (Ground floor foyer)</i>		
11:00 – 11:35	O16	Gustavo Scuseria (Houston, TX, U.S.A.) <i>Hybrid and Macroconfiguration Coupled-Cluster Methods</i>	Chair: Zvonimir Maksic (Zagreb, Croatia)
11:35 – 12:10	O17	Mark S. Gordon (Ames, IA, U.S.A.) <i>Exploring Energy Landscapes: From Coupled Cluster to Model Potentials</i>	Chair: Michael E. Colvin (Merced, CA, U.S.A.)
12:10 – 12:45	O18	Kimihiko Hirao (Tokyo, Japan) <i>Molecular Theory for Large Systems</i>	Chair: Peter A. Schwerdtfeger (Auckland, Australia)
12:45 – 14:30	<i>Lunch break (Platan Restaurant)</i>		
Section: Electron Correlation (Star Auditorium)			
14:30 – 15:05	O19	Wesley D. Allen (Athens, GA, U.S.A.) <i>State-Specific Multireference Coupled Cluster Theories: Chemical Applications of New Production-Level Methods and High-Order Excitation Studies of Model Systems</i>	Chair: Jack Simons (Utah, U.S.A.)
15:05 – 15:40	O20	Wim Klopper (Karlsruhe, Germany) <i>Quintuple-Zeta Quality Correlation Energies with Triple-Zeta Basis Sets</i>	Chair: Miroslav Urban (Bratislava, Slovakia)
15:40 – 16:15	O21	Rodney J. Bartlett (Gainesville, FL, U.S.A.) <i>Is There Something Better than CCSD(T) for Molecular Applications?</i>	Chair: Josef Paldus (Waterloo, Canada)
16:15 – 16:45	<i>Coffee break</i>		
16:45 – 17:20	O22	Martin Head-Gordon (Berkeley, CA, U.S.A.) <i>New Electronic Structure Methods for Large Reactive Radicals and Diradicals</i>	Chair: Elfriede Kraka (Stockton, CA, U.S.A.)
17:20 – 17:55	O23	Jozef Noga (Bratislava, Slovakia) <i>MP2-R12 Versus Dual Basis MP2 Theory</i>	Chair: Garnet Chan (Ithaca, NY, U.S.A.)
18:30 – 21:00	<i>Poster session (Jasmine Room)</i>		

FRIDAY, June 1, 2007

Section: Structure and Spectroscopy (Star Auditorium)			
9:00 – 9:20	H3	Ian M. Mills (Reading, United Kingdom)	Chair: James E. Boggs (Austin, TX, U.S.A.)
<i>Quantum Chemical Computation of Force Fields and Molecular Spectra</i>			
9:20 – 9:55	O24	John F. Stanton (Austin, Texas, U.S.A.)	Chair: James E. Boggs (Austin, TX, U.S.A.)
<i>NO₃: The Molecule without a Structure</i>			
9:55 – 10:30	O25	Eric Oldfield (Urbana-Champaign, IL, U.S.A.)	Chair: Jürgen Gauss (Mainz, Germany)
<i>How Peter Pulay Helped Me Become an Applied Quantum Chemist</i>			
10:30 – 11:00	Coffee break (Ground-floor foyer)		
11:00 – 11:35	O26	David C. Clary (Oxford, U.K.)	Chair: Peter R. Taylor (Warwick, United Kingdom)
<i>Quantum Calculations on the Conformations of Biomolecules</i>			
11:35 – 12:10	O27	Sharon Hammes-Schiffer (University Park, PA, U.S.A.)	Chair: Miriam Karni (Haifa, Israel)
<i>Nuclear-Electronic Orbitals Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations</i>			
12:10 – 12:45	O28	Pavel Rosmus (Marne la Vallée, France)	Chair: Josef Michl (Boulder, CO, U.S.A.)
<i>Nuclear Dynamics in Degenerate Electronic States: Spectroscopy and ab Initio Calculations for Pseudorotating B₃ and C₃⁺</i>			
12:45 – 15:05	Lunch break (Platan Restaurant)		
15:05 – 15:40	O29	Werner Kutzelnigg (Bochum, Germany)	Chair: Pekka Pyykkö (Helsinki, Finland)
<i>Which Masses are Vibrating or Rotating in a Molecule?</i>			
15:40 – 16:15	O30	Frederick R. Manby (Bristol, United Kingdom)	Chair: Peter J. Knowles (Cardiff, United Kingdom)
<i>Extension of Gas-Phase Methods to Condensed Phase Problems</i>			
16:15 – 16:50	O31	Martin Quack (Zürich, Switzerland)	Chair: Gernot Frenking (Marburg, Germany)
<i>Recent Results in Molecular Quantum Chemical Kinetics from Spectroscopy: Symmetry Conservation and Beyond</i>			
19:30 – 22:30	Conference banquet – cruise on the Danube		

SATURDAY, June 2, 2007

Section: Dynamics and Reactions (Star Auditorium)					
9:00 – 9:20	H4	Gabriel Balint-Kurti (Bristol, United Kingdom)	Chair: Michael E. Robb (London, United Kingdom)		
		<i>Molecular Dynamics and Quantum Chemistry</i>			
9:20 – 9:55	O32	Michele Parrinello (Zürich, Switzerland)	Chair: Michael E. Robb (London, United Kingdom)		
		<i>Second Generation Car-Parrinello Method</i>			
9:55 – 10:30	O33	Hans Lischka (Vienna, Austria)	Chair: Ron Shepard (Argonne, IL, U.S.A.)		
		<i>Watching the Motion of Molecules in Excited States: From Ethylene to Retinal Models and Excited-State Intramolecular Proton Transfer</i>			
10:30 – 11:00	<i>Coffee break (Ground floor foyer)</i>				
11:00 – 11:35	O34	H. Bernhard Schlegel (Detroit, MI, U.S.A.)	Chair: Stefan Grimme (Münster, Germany)		
		<i>Exploring Potential Energy Surfaces with ab Initio Molecular Dynamics</i>			
11:35 – 12:10	O35	William C. Swope (San Jose, CA, U.S.A.)	Chair: Jerzy Leszczynski (Jackson, MS, U.S.A.)		
		<i>Protein Folding Studied by Computer Simulation on Blue Gene at IBM</i>			
12:10 – 12:45	O36	Hans-Joachim Werner (Stuttgart, Germany)	Chair: Kenneth Ruud (Tromsø, Norway)		
		<i>The Effect of Local Approximations on the Calculation of Molecular Properties and Reaction Energies</i>			
12:45 – 14:30	<i>Lunch break (Platan Restaurant)</i>				
Section: Techniques of MQM (Star Auditorium)					
14:30 – 15:05	O37	Jan M. L. Martin (Rehovot, Israel)	Chair: Thom H. Dunning (Champaign, IL, U.S.A.)		
		<i>W4 Theory: Confident Sub-kJ /mol Accuracy Computational Thermochemistry</i>			
15:05 – 15:40	O38	Laura Gagliardi (Geneva, Switzerland)	Chair: Manuel Yáñez (Madrid, Spain)		
		<i>Hybrid Functionals for Solid-State Systems</i>			
15:40 – 16:15	O39	C. David Sherrill (Atlanta, GA, U.S.A.)	Chair: Anna Krylov (Los Angeles, CA, U.S.A.)		
		<i>Multiconfigurational Quantum Chemistry for Actinide Containing Systems: From Isolated Molecules to Condensed Phase</i>			
16:15 – 16:45	<i>Coffee break (Ground floor foyer)</i>				
16:45 – 17:20	O40	Troy van Voorhis (Cambridge, MA, U.S.A.)	Chair: Alejandro Toro-Labbe (Santiago, Chile)		
		<i>Exploring Electronic Structure with Constrained Density Functional Theory</i>			
17:20 – 17:55	O41	Ming Wah Wong (Singapore)	Chair: Kwang S. Kim (Pohang, Korea)		
		<i>$\pi^* - \pi^*$ Interaction in Sulfur and Oxygen Chemistry</i>			
17:55 – 18:30	O42	Krzysztof Wolinski (Lublin, Poland)	Chair: Frank Neese (Bonn, Germany)		
		<i>Geometry Optimization and Vibrational Harmonic Frequency Calculations with a Dual Basis Set Approach</i>			
18:30 – 21:00	<i>Poster session (Jasmine Room)</i>				

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SUNDAY, June 3, 2007

Section: Techniques of MQM (Star Auditorium)			
9:00 – 9:35	O43	István Mayer (Budapest, Hungary) <i>Energy Partitioning Schemes</i>	Chair: Attila G. Császár (Budapest, Hungary)
9:35 – 10:10	O44	János Ángyán (Nancy, France) <i>Density Functionals with Range Separation: The DFT Heaven without Jacob's Ladder</i>	Chair: Attila G. Császár (Budapest, Hungary)
10:10 – 10:45	O45	Ellak von Nagy-Felsobuki (Callaghan, Australia) <i>Ab Initio Rovibrational Spectrum of BeH_2^{2+} Using IC-MRCI Property Surfaces</i>	Chair: Attila G. Császár (Budapest, Hungary)
10:45 – 11:15	<i>Coffee break (Ground floor foyer)</i>		
11:15 – 11:50	O46	George Bacsikay (Sydney, Australia) <i>Quantum Chemical Computations of Spectroscopic Constants, Oscillator Strengths, and Radiative Lifetimes</i>	Chair: Péter G. Szalay (Budapest, Hungary)
11: 50 – 12:25	O47	Gyula Tasi (Szeged, Hungary) <i>Titles to be announced</i>	Chair: Péter G. Szalay (Budapest, Hungary)
12: 25 – 13:00	O48	Peter Pulay (Fayetteville, AR, U.S.A.) <i>Large Coupled Cluster Calculations on Inexpensive Parallel Computers: Applications to Weak Interactions</i>	Chair: Péter G. Szalay (Budapest, Hungary)
13:00 – 13:10	Closing ceremony (Star Auditorium) Géza Fogarasi, conference organizer		

HISTORICAL TALKS

Early Developments of Analytic Techniques

Wilfried Meyer

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The development of analytic gradient techniques in electronic structure theory carries the name of Peter Pulay. His groundbreaking idea (which may look simple in retrospect) was in fact a very daring proposal which he turned into an eminently successful computational approach that determined a decade of quantum chemical method development. In spring 1968 Peter Pulay was on a research visit in Germany and we met in Munich. We agreed to jointly develop a program with an SCF gradient part and a CI part, the first version of MOLPRO. So I was witness to Peter deriving the full theory of analytical SCF energy gradients [1] and simultaneously developing its efficient program implementation. This led to the first exemplary applications [2] and provided the basis for more routine applications [3,4] even after Peter had returned to Budapest. There he adapted the gradient technique to semi-empirical methods [5]. It was soon extended to cover open-shell [6] and MCSCF cases as described in Peter's first review article [7]. The analytic derivative technique gained real impact on the research field only after Peter's sabbatical visits to Austin and Berkeley in 1976. His more powerful TEXAS program [8] made applications to larger molecules possible. This finally started an avalanche of method developments towards more sophisticated electron structure methods, higher order energy derivatives and gradient based searches on potential energy surfaces. Analytic derivatives are now part of any decent electronic structure program and are indispensable for a wide range of applications.

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Density Functional Theory and Plane Waves

Nicholas C. Handy

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Cambridge, United Kingdom*

The arrival of DFT has made a huge impact on computational chemistry. A brief analysis of progress in the last 15 years will be given (LDA, GGA, Hybrid, Attenuated Hybrid, Hybrid with MP2). Pulay's significant paper on the Fourier Transform Coulomb (FTC) method will be analysed.

Quantum Chemical Computation of Force Fields and Molecular Spectra

Ian M. Mills

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In this talk I shall review the significance of Peter Pulay's contributions in the field of *ab initio* calculations in molecular quantum mechanics and quantum chemistry, particularly in relation to the calculation of force fields and molecular spectra from gradient calculations of the potential energy surface. My own research interests in force constant calculations were based on the calculation of force constants from experimental data on molecular vibrations, isotopic shifts, and vibration-rotation interactions. Peter's contributions from quantum chemistry calculations provided a unifying theme to theoretical and empirical approaches to molecular force fields.

Molecular Quantum Dynamics

Gabriel G. Balint-Kurti

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The pivotal role of *ab initio* analytic derivatives in modern molecular quantum dynamics will be discussed, with examples from transition state theory, variational RRKM [1] theory and quantum reactive wavepacket applications. The application of diagonalisation techniques, developed for electronic configuration interaction calculations, to problems in molecular vibrational spectroscopy will be outlined [2]. A brief review of time-dependent molecular quantum dynamics as applied to photodissociation processes and reactive scattering will be given [3-5].

References:

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INVITED SPEAKERS

Clusters of Boron: Experimental and DFT Treatment of B₁₂-B₃₀

Nathan R. M. Crawford, Reinhart Ahlrichs, Esther Oger,

Rebecca Kelting, Patrick Weis, and Manfred M. Kappes

*Institut für Physikalische Chemie, Universität Karlsruhe
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We systematically investigate boron clusters from B₁₂ to B₃₀ together with their cations (for some recent investigations see references 1-3). Structures were optimized using a hybrid ab initio genetic algorithm[4] using a small SVP basis and the BP-86 functional. The final population of low energy structures and their cations were then re-optimized with the larger def2-TZVPP basis (11,6,2,1)[5,3,2,1] and the TPSS functional. The program system TURBOMOLE was used throughout. Structures so obtained were then used to determine the cation cross sections for gas phase ion mobility experiments, similar to a previous investigation of gold clusters [5]. At this stage, the computed lowest energy structures fit well with experimental data. Clusters of boron show an unusually rich zoo of low energy structures, often with 10 isomers within an eV of the minimum. A notable exception being B₂₀+, an S4-symmetry cylinder (derived from the D_{10h}-symmetry neutral B₂₀) where the minimum energy isomer is over 1 eV more stable than any other structure. The dominant motif is of B₃ triangles tessellated into cylinders, planes (be they flat, curved, or puckered), and incomplete hollow spheres. There is a remarkable absence of space filling structures, quite different from Al or Ga clusters. The drift experiments show the presence of two isomers for B₂₆ and above, where we begin to see irregular 3D structures. The relative utility of the genetic algorithm will be critically assessed. For B4n, the double rings are notably stable. The DFT calculations provide strong indications of the multi-reference nature of their electronic structures.

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State-Specific Multireference Coupled Cluster Theories: Chemical Applications of New Production-Level Methods and High-Order Excitation Studies of Model Systems

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Simple closed-form expressions are derived through arbitrary order for the “same vacuum” renormalization terms that arise in state-specific multireference coupled cluster (MRCC) theories. The first production-level code (**psimrcc**) has then been written for a state-specific and rigorously size-extensive multireference coupled cluster singles and doubles theory first proposed by Mukherjee (MkCCSD). Our code is also capable of evaluating analogous Brillouin-Wigner multireference energies (BWCCSD), including *a posteriori* size-extensivity corrections. Using correlation-consistent basis sets (cc-pVXZ, $X = D, T, Q$), MkCCSD and BWCCSD were first tested and compared on two classic multireference problems: (1) the dissociation potential curve of molecular fluorine (F_2), and (2) the structure and vibrational frequencies of ozone. The MKCCSD method is generally superior to Brillouin-Wigner theory in predicting energies, structures, and vibrational frequencies. Although MkCCSD theory greatly improves upon single-reference CCSD for the geometric parameters and a_1 vibrational frequencies of ozone, the antisymmetric stretching frequency $\omega_3(b_2)$ remains pathological and cannot be properly treated without the inclusion of connected triple excitations. Next, multireference MkCCSD results were obtained for the singlet-triplet splittings in *ortho*-, *meta*-, and *para*-benzyne, coming within 1.5 kcal mol⁻¹ of experiment in all cases. Several benchmarks we have executed reveal that MkCCSD is exceptionally accurate in determining singlet-triplet splittings if applied to the $M_S = 0$ components of *both* states. Finally, an arbitrary-order string-based code was written to perform comprehensive high-order excitations ($n > 2$) studies on the H_4 , P_4 , BeH_2 , and H_8 models with complete excitations ranging up to hextuples. Comparison is then made to corresponding single-reference (SR) coupled cluster and full configuration interaction (FCI) results.

Density Functionals with Range Separation: The DFT Heaven without Jacob's Ladder

János Ángyán

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There are a few but important cases where standard density functionals, situated on the first few rungs of “Jacob’s ladder”, fail. One can cite as example London dispersion forces, barriers of atom transfer reactions, structure and energetics of transition metal compounds or donor-acceptor type intermolecular complexes. The origin of most of these problems is rooted in the incorrect asymptotic behavior of the exchange-potential on the one hand, and in the incomplete account of certain kinds of electron correlations, like of the long-range dynamic correlation (van der Waals systems) or of the non-dynamic correlations (intrinsically multideterminant systems), on the other hand.

These difficulties can be handled efficiently in the framework of a hybrid approach, where electron repulsion is partitioned to a short- and a long-range component in the Hamiltonian [1]. Treating the long-range interactions explicitly and short-range interactions by appropriately designed functionals, one obtains an effective Hamiltonian corresponding to a weakly interacting system. In contrast to the non-interacting Kohn-Sham model, the solution of this range-separated model is necessarily in a multi-determinant form, and requires the use of standard WFT approaches, like CI or MBPT [2,3]. In the absence of explicit short-range electron repulsion, these latter methods converge much faster with respect to the one- and many-electron basis.

Significant improvement can be achieved even at the simplest level, where the WFT treatment is limited to the exchange and the full range of correlation is described by a functional. In the absence of long-range self-interaction errors, the dissociation of symmetric radical cations [3], the barrier of atom transfer reactions [4] and the charge transfer in donor-acceptor complexes is significantly improved. In the case of London dispersion forces an explicit treatment of long-range correlations, e.g. at the MP2 level, is absolutely necessary. The performance of this methodology is illustrated by rare gas [2,5] and alkaline-earth [6], benzene and dinitrogen dimers.

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Quantum Chemical Computations of Spectroscopic Constants, Oscillator Strengths and Radiative Lifetimes

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High level *ab initio* calculations, using multi-reference configuration interaction (MRCI) techniques, have been carried out to investigate the spectroscopic properties of the singlet Phillips ($A^1\Pi_u \leftarrow X^1\Sigma_g^+$) and the triplet Swan ($d^3\Pi_g \leftarrow a^3\Pi_u$), Ballik-Ramsay ($b^3\Sigma_g^- \leftarrow a^3\Pi_u$) and $d^3\Pi_g \leftarrow c^3\Sigma_u^+$ transitions of C_2 . The MRCI expansions are based on full-valence CASSCF reference states and utilize the aug-cc-pV6Z basis set to resolve valence electron correlation. Core and core-valence correlation and scalar relativistic energy corrections were also incorporated in the computed potential energy surfaces. Non-adiabatic and spin-orbit effects were explored, but found to be of negligible importance in the calculations. The predicted spectroscopic constants are typically within 0.1 – 1 % of experiment. The calculated radiative lifetimes also compare very well with the available experimental data. Oscillator strengths are reported for all systems: f_{vv^*} where $0 \leq v \leq 5$.

Structure, Dynamics, and Properties of Aromatic Materials Based on Corannulene

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Fullerenes, and Nanotubes all stem from sheets of sp^2 hybridized carbon arranged in aromatic/benzenoid subunits. Corannulene is a fundamental structure in this family as it represents the insertion of a 5-membered ring „imperfection“ into the two-dimensional lattice of graphite, which results in a warping or bowing of the sheet leading through Euler’s theorem to carbon tubes and spheres. This fundamental unit is rich in structural, dynamic and physical features that challenge modern quantum mechanical methods. The size of some corannulene derivatives places a strain on resources and raises the issue of computational strategy (*i.e.*, parallel, cluster, or grid). The response to basis set, correlation and multi-state factors is non-trivial when considering structural, dynamic and physical aspects as an integrated problem package. This talk will describe our computational approaches, predictions made, and experimental comparisons for the general structure of corannulene derivatives; the structure dynamic correlation of bowl depth and energy to inversion; NMR and UV spectroscopic analysis; and the complex reactive processes of highly substituted derivatives.

Is There Something Better Than CCSD(T) For Molecular Applications?*

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The remarkable success of CCSD(T) in molecular applications is well known, despite it being a hybrid of CCSD with triple excitations estimated from MBPT. Because of its perturbative element, it will inevitably fail as bonds are broken, unless the single determinant reference function itself is a correctly separating UHF solution, and even for such cases, the spin recoupling regions of a potential curve tend to not offer an accurate description. Besides entire potential energy surfaces, this also raises potential issues with the description of transition states as such bonds start to be broken. Some years ago it was proposed to base a model similar to CCSD(T) on the functional of CC theory, $\langle 0|(1+\Lambda)\exp(-T)\Lambda\exp(T)|0\rangle$, termed ACCSD(T) (S. A Kucharski, and R. J. Bartlett, *J. Chem. Phys.* **108** 5243 (1998). Like CCSD(T) it is formally perturbative, but behaves much better as a function of R because of the role of Λ . Like CCSD(T) this is an $\sim n^7$ method, but does require the evaluation of Λ along with T. Analytical gradients have been developed for this method and added to ACES II to make a wide range of applications possible. A variety of results will be presented.

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Techniques for Improved Sampling and Free Energies Estimation in Examining Reaction Pathways for Macromolecular Systems

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This presentation will focus on our recent attempts techniques to include sampling and to estimate entropic contributions while examine complex processes in macromolecular systems using ab initio QM/MM methods. The methods are primarily designed to examine protein conformational change and enzyme catalysis. Methods for improving sampling by combining SGLD and REX will be presented with some examples. This is coupled with our replica/path methods for pathway searching and for estimating entropy contributions. Finally, techniques for estimating vibrational free energies using a formal splitting of the vibrational partition function into a subsystem and and environment part will be presented

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Quantum Calculations on the Conformations of Biomolecules

David C. Clary

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This talk will describe work done in our group on using quantum methods to simulate the dynamics of small biomolecules in the gas phase.

Calculations using the diffusion Monte Carlo method will be summarised that indicate the importance of quantum effects on the structures of molecular clusters and biomolecules.

Calculations performed with the Torsional Path Integral (TPI) method will also be presented. The TPI method has the potential to be a powerful simulation method for biomolecules. It allows all torsional degrees of freedom to be coupled together in quantum calculations of free energies and biomolecular conformations as a function of temperature.

The calculations were done by David Benoit, Massimo Mella, Tommy Miller and Yvette Sturdy.

Multiconfigurational Quantum Chemistry for Actinide Containing Systems: From Isolated Molecules to Condensed Phase

Laura Gagliardi

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In this lecture I will describe our latest achievements in the prediction of novel chemical bonds and chemical species, including the multiple bond in the early-diactinide series [1] and some novel inorganic compounds containing the diuranium moiety [2]. The results of a combined experimental and theoretical study of a novel uranium polyhydride compound, with a large number of H atoms around U, $\text{UH}_4(\text{H}_2)_8$, [3] will also be described. In nature most of actinide chemistry occurs in solution. We try to combine *ab initio* quantum chemistry with classical molecular dynamics simulations in order to understand the behavior of highly charged ions in solution. Our recent studies of uranyl [4] and Cm(III) [5] in water will be presented. It seems that nowadays it is possible to understand the chemical bond in the entire periodic table by means of quantum chemical methods.

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Electron Correlation: A Hungarian Dance in Three Movements

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Several two-electron distributions can be extracted from a many-electron wavefunction, via the Wigner distribution $W_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2)$. Two of these, the Position and Momentum intracules, are well known and have been discussed by many authors. In recent years, we have introduced six others, the Omega, Wigner, Lambda, Action, Dot and Angle intracules.

The physics of electron correlation depends less on the *absolute* positions and momenta of two electrons than on their relative position $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and relative momentum $\mathbf{p}_{12} = \mathbf{p}_1 - \mathbf{p}_2$. One also suspects that the absolute directions of the vectors \mathbf{r}_{12} and \mathbf{p}_{12} are less important than their magnitudes r_{12} and p_{12} but that the dynamical angle θ_{uv} between them may be significant. It is therefore plausible that most of the important information in $W_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2)$ is captured by the three key variables, r_{12} , p_{12} and θ_{uv} , whose joint probability density is

$$\begin{aligned}\Omega(u, v, \omega) &= \int W_2(r_1, r_2, p_1, p_2) \delta(\theta_{uv} - \omega) \delta(r_{12} - u) \delta(p_{12} - v) dr_1 dr_2 dp_1 dp_2 \\ &= \frac{1}{8\pi^3} \rho_2(r, r+q, r+u+q, r+u) e^{iq\cdot v} \delta(\theta_{uv} - \omega) dr dq d\Omega_u d\Omega_v\end{aligned}$$

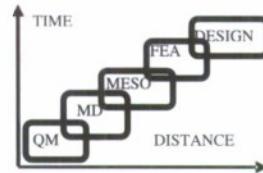
where Ω_u and Ω_v are the angular parts of \mathbf{u} and \mathbf{v} , respectively, and ρ_2 is the spinless reduced second-order density matrix. We have called this novel function the Omega intracule.

What use can be made of this function? One of the most exciting possibilities is as the foundation of radical new approaches to the electron correlation problem. In standard methods, correlation effects are treated by writing the wavefunction as a lengthy linear combination of determinants. However, this is inefficient and quickly leads to great computational expense. In contrast, a model based on intracules can be physically motivated and much less expensive and we have recently proposed that the correlation energy can be estimated from the Omega intracule through

$$E_c = \int \int \int \Omega(u, v, \omega) G(u, v, \omega) d\omega dv du,$$

where $G(u, v, \omega)$ is a universal function that we call the Omega correlation kernel. In addition, there exist a hierarchy of simpler models based on, for example, the Wigner and Lambda intracules.

In my lecture, I will outline the theory, discuss its computational requirements, and present results for a variety of atomic and molecular systems.



First Principles Approaches to Design of Materials with Applications to Catalysis, Nanoelectronics, Fuel Cells, and Pharma

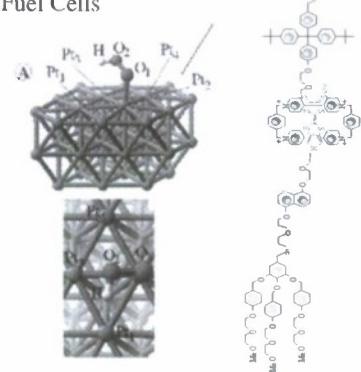
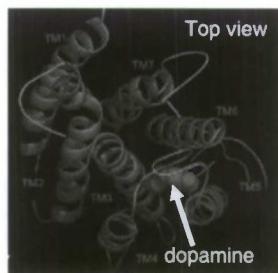
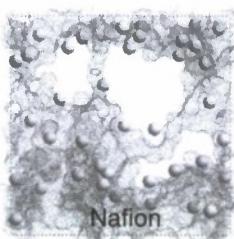
William A. Goddard, III

*Charles and Mary Ferkel Professor of
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Advances in theoretical and computational chemistry are making it practical to consider fully first principles (*de novo*) predictions of important systems and processes in the Chemical, Biological, and Materials Sciences. Our approach to applying first principles to such systems is to build a hierarchy of models each based on the results of more fundamental methods but coarsened to make practical the consideration of much larger length and time scales. Connecting this hierarchy back to quantum mechanics enables the application of first principles to the coarse levels essential for practical simulations of complex systems.

We will highlight some recent advances in methodology and will illustrate them with recent applications to materials problems involving Catalysis, Nanoelectronics, Fuel Cells and pharma selected from

- Mechanism Organometallic reactions (Wacker process, IBX, Tsuji Allylation)
- Mechanism of Heterogeneous reactions: ammonoxidation on MMO
- Predictions of 3D structures of G Protein Coupled Receptors (GPCRs)
- Predictions of selective agonists and antagonists for GPCRs
- Conductance properties of Nanoelectronic switches and carbon nanotube interconnects
- De novo Force Fields (from QM) to describe reactions and phase transitions (ReaxFF)
- New membranes for PEMFC and predictions of proton transport across catalyst-PEM interface
- Simulations of Solid Oxide and Solid Acid membranes for Fuel Cells
- Domain switching in BaTiO_3 ferroelectrics
- The plaquette polaron theory of cuprate superconductors



Exploring Energy Landscapes: From Coupled Cluster to Model Potentials

Mark S. Gordon

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One of the many contributions of Peter Pulay is the vast research he has done that enables the efficient exploration of complex potential energy surfaces. This talk will examine the study of potential energy landscapes from several perspectives. These include the development of strategies for determining accurate vibrational spectra, methods for employing massively parallel computers to greatly expand the sizes of accessible problems that one can treat with accurate electronic structure methods, and sophisticated model potentials that accurately describe a broad array of intermolecular forces. Example applications will be presented that illustrate each of these developments.

Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations

Sharon Hammes-Schiffer

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Recent advances in the development of the nuclear-electronic orbital (NEO) approach will be presented. In the NEO approach, both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions, and the variational method is utilized to minimize the energy with respect to all molecular orbitals as well as the centers of the nuclear basis functions. This approach is particularly useful for the description of hydrogen transfer and hydrogen bonding. For these applications, the hydrogen nuclei, as well as all electrons, are treated quantum mechanically to include nuclear quantum effects such as zero point energy and hydrogen tunneling. The multiconfigurational self-consistent-field (NEO-MCSCF), nonorthogonal configuration interaction (NEO-NOCI), second-order perturbation theory (NEO-MP2), and density functional theory (NEO-DFT) methods have been developed to include correlation effects. Electron-proton dynamical correlation is highly significant because of the attractive electrostatic interaction between the electron and the proton. An explicitly correlated Hartree-Fock (NEO-XCHF) scheme has been formulated to include explicit electron-proton correlation directly into the nuclear-electronic orbital self-consistent-field framework with Gaussian-type geminal functions. In contrast to previous approaches, which produce nuclear wavefunctions that are too localized and severely overestimate hydrogen vibrational frequencies, the NEO-XCHF method provides accurate nuclear wavefunctions and hydrogen vibrational frequencies. This method is computationally practical for many-electron systems because only electron-proton correlation is treated explicitly. The strengths and challenges of these approaches will be discussed, and applications to hydrogen transfer and hydrogen bonding systems will be presented.

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New Electronic Structure Methods for Large Reactive Radicals and Diradicals

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Electronic structure methods form the basis for first principles characterizations of the potential energy surfaces that underlie molecular properties, chemical reaction mechanisms, and nuclear dynamics. Despite tremendous progress, the most ubiquitous electronic structure methods, based on density functional theory (DFT), exhibit failures for molecules with strong correlations, some types of radicals, and systems where dispersion interactions are important. At the same time, the most accurate electronic structure methods, based on coupled cluster theory, remain too computationally demanding to enable the routine treatment of large molecules. In this talk, I will discuss two classes of electronic structure methods under development in my group that offer the prospect of bridging this gap. First are methods that attempt to provide a reasonable description of strongly correlated electrons by systematically approximating the Schrodinger equation in the space of valence bonding and antibonding orbitals that defines a complete active space (CAS). Accurate approximations to CAS calculations are possible at modest computational expense, and I will discuss the physical and mathematical content of these approximations, and their performance on practical problems. Second is a new approach that correctly and inexpensively recovers dispersion interactions, without either excessive spin-contamination for radicals (as plagues traditional unrestricted Hartree-Fock-based methods), or the difficulties of self-interaction that can affect DFT calculations of radicals. The performance of this approach for relative energies, structures, and frequencies will be assessed, both for closed shell molecules, radicals, as well as some cases which exhibit pathological failures at both the DFT and MP2 levels of theory.

The Calculation of Molecular Properties of Large Systems

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With recent developments in theory and implementation, Hartree–Fock and Kohn–Sham self-consistent-field methods can now be applied to large molecular systems, at a cost that scales linearly with system size. In the present talk, recent developments are reviewed, with emphasis on the optimization of the energy and the calculation of properties such as frequency-dependent polarizabilities and excitation energies for large molecules.

Molecular Theory for Large Systems

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With the emergence of peta-scale computing platforms we are entering a new period of modeling. The computer simulations can be carried out for larger, more complex, and more realistic systems than ever before. The evaluation of Coulomb integrals is very often the most time consuming step for DFT with GGA functionals. A new linear scaling method has been developed for the fast evaluation of Coulomb integrals. The Coulomb potential is expanded in the mixed Gaussian and finite-element auxiliary functions. Then Coulomb integrals can be evaluated by solving the Poisson equation. The method realizes a linear scaling with system size and makes molecular quantum calculations affordable for very large systems involving several thousands of basis functions. Recently we have developed the dual-level approach to DFT. The scheme is based on the low sensitivity of the electron density to the choice of the functional and the basis set. The dual-level DFT works quite well and the large reduction of the computer resources can be achieved. Hybrid functional can now be applied to very large systems. The first-order molecular properties are well predicted by GGA functionals. However, induced or response properties require correction for the asymptotic behavior. The failure arises from the wrong long range behavior due to the local character of the approximate exchange- correlation functionals. By splitting the Coulomb interaction into short-range and long-range components, we have proposed a new hybrid functional with correct long-range electron- electron interactions. Hybrid GGA has good energetics, good Rydberg behavior, good CT predictions, and good optical response. Van der Waals interactions are also described accurately. The scheme was applied to planar aromatic systems (dimers and trimers of coronene, circum coronene, and circum circum coronene) to estimate pi-stacking energies.

First-Principles Simulations of Liquids

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The combination of electronic structure methods, mostly based on density functional theory, with molecular dynamics and Monte Carlo sampling methods have made the study of liquids and solutions from first-principles possible. These methods overcome the limitations of pre-computed potentials and have made important contributions to theory and experiment. They also allow for tests of electronic structure methods and density functionals in a new and challenging area. However, the limited time and size scale available in the simulations are a serious problem. In addition, the interplay of the classical dynamics of the nuclei with the electronic structure method cause new problems absent in force field calculations. Whereas most of the earlier calculations in this field were made using plane wave basis sets, newer approaches rely more and more on atomic basis sets. We will review recent progress in the simulation of liquids using algorithms and basis sets adapted for the Gaussian and plane waves method.

Coupled-Cluster Gradients and Beyond

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The development of analytic derivatives for highly correlated ab initio methods is reviewed. In particular, the theory of analytic first and second derivatives for general coupled-cluster (CC) and configuration-interaction (CI) models is discussed including multi-reference and approximate CC methods as well as excited-state CC treatments (linear-response CC). Efficient implementation of the considered approaches is possible using our string-based many-body technique. The development of analytic third derivatives is also considered. The applicability of the implemented analytic derivatives is demonstrated for molecular properties with special regard to geometries, vibrational frequencies, NMR chemical shifts, and electrical polarizabilities. Our results suggest that inclusion of higher-order correlation is desirable for determination of molecular properties with quantitative accuracy.

Quintuple-Zeta Quality Correlation Energies with Triple-Zeta Basis Sets

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The explicitly-correlated coupled-cluster method CCSD(T)(R12) [1,2] has been extended to include F12 Slater-type geminal basis functions [3], which decay exponentially with the interelectronic distance r_{12} , and which reproduce the global form of the average Coulomb hole more accurately than linear r_{12} correlation factors [4,5]. The new CCSD(T)(F12) method has been implemented using the strong-orthogonality projector of Ansatz 2 and the convergence of the correlation energy with the size of the orbital basis set has been studied [6]. The convergence was found to be rapid. Typically, 98% of the basis-set limit correlation energy was recovered using triple-zeta orbital basis sets. The performance for reaction enthalpies has been assessed using a test set of 15 reactions involving 23 small molecules including COCl_2 , SO_3 , HCONH_2 , C_2H_6 and others. Quintuple-zeta quality results were obtained for total and relative correlation energies using a triple-zeta basis set [6].

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Which Masses are Vibrating or Rotating in a Molecule?

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Going back to Born, there is a hierarchy (or rather a family of hierarchies) of approximations, that lead from the Born–Oppenheimer (BO) separation via the adiabatic approximation to an exact (non-adiabatic) theory. This highest level is necessary for hydrogen-containing small molecules, if one strives at 'spectroscopic accuracy'. On the BO and adiabatic levels only the nuclei participate in rotational or vibrational motions. The obvious participation of the electrons in these motions must so far be treated as a non-adiabatic effect. Unfortunately the non-adiabatic corrections to vibrational frequencies are of the same order of magnitude as the adiabatic ones. In this lecture it is shown that in non-degenerate situations the participation of the electrons in rotation and vibration is the dominant nonadiabatic effect, and that electrons participate in rotation much less than in vibration. As a model case H_2^+ is studied, for which effective rotational and vibrational masses are derived. Conclusions for arbitrary molecules are drawn.

Watching the Motion of Molecules in Excited States: From Ethylene to Retinal Models and Excited-State Intramolecular Proton Transfer

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The theoretical treatment of the photodynamics of molecular systems is very challenging. One major problem is the accurate computation of excited-state surfaces and intersection seams. Even after having obtained an overview of the energy surfaces by means of characteristic points (energy minima, saddle points and minima on the crossing seam), the prediction of the dynamical behavior of the molecular system based on these quantities alone will be very difficult.

It is one purpose of this talk to demonstrate the need for explicit dynamics simulations in comparison to the just-mentioned standard static analysis. The calculations are based on the program package NEWTON-X, which has been developed in our group allowing nonadiabatic surface-hopping dynamics calculations using on-the-fly techniques. This program package is structured in a modular way allowing the incorporation of practically any quantum chemical program package producing at least analytic energy gradients. Currently, implementations are available for COLUMBUS (MRCI energy gradients and nonadiabatic coupling vectors), TURBOMOLE (RI-CC2 and TDDFT energy gradients) and MOPAC2000 (FOMO-CI).

In a first set of examples, the photodynamics of polar π bonds using the series of ethylene, fluorethylene and the formiminium cation is discussed. The calculations show that in addition to the expected torsion around the double bond other processes such as bipyramidalization and bond dissociation are of relevance. In extension of the formiminium cation, the photodynamics of protonated Schiff bases containing 3 and 4 double bonds is discussed with the aim to obtain detailed insight into the dynamics of retinal models. Mechanical restrictions were applied to the terminal hydrogen atoms in order to simulate spatial effects of a protein environment.

As a set of completely different examples, the excited-state intramolecular proton transfer in the chelate systems 2-(2'-Hydroxyphenyl)benzothiazole (HBT) and 10-hydroxybenzoquinoline (HBQ) has been studied using adiabatic TDDFT dynamics. The computed proton transfer times are in excellent agreement with experimental values reported in the group of E. Riedle (Munich). Additionally, for the keto form of HBT an interesting torsional mode has been found, which leads to a conical intersection with the ground state and to an ultrafast decay channel with a decay time of about 1 ps.

Extension of Gas-Phase Methods to Condensed Phase Problems

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The great achievements of quantum chemistry in recent decades mean that for small-molecule gas-phase chemistry, computation of experimentally relevant quantities (rates, to name but one example) can be performed to high accuracy. Moreover, the existence of well established hierarchies of approximation means that agreement with experiment can be improved systematically. The situation is not so mature in the context of condensed phase problems, and in this talk I will describe efforts underway in Bristol to extend the successful hierarchies of gas-phase electronic structure theory into the domain of condensed phase chemistry.

W4 Theory: Confident Sub-kJ/mol Accuracy

Computational Thermochemistry

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We will discuss the theoretical underpinnings and applications of W4 theory [J. Chem. Phys. 125, 144108 (2006)], our next-generation computational thermochemistry method. By comparison with very accurate experimentally derived ATcT (Active Thermochemical Tables, as developed by Branko Ruscic et al.) data for several dozen key species, we were able to establish that W4 theory achieves an RMSD in the total atomization energies of about 0.3 kJ mol^{-1} , and a 95% confidence interval well below the 1 kJ mol^{-1} limit. Yet, W4 is still devoid of any parameters derived from experiment. While many factors contribute to the success of W4 theory (such as separate partial-wave extrapolations for singlet-coupled and triplet-coupled pairs, very large basis sets, improved treatments of inner-shell correlation and scalar relativistics, and inclusion of a diagonal Born–Oppenheimer correction), the key factor is the post-CCSD(T) “level correction”. Basis set convergence of various post-CCSD(T) contributions, $T_3 - (T, (Q), T_4 - (Q), T_5, \text{etc.})$, will be discussed in some detail. Finally, as an illustrative application, we will offer arguments in favor of the revision of several atomic heats of formation in the first and second rows of the Periodic Table (notably boron, aluminum, silicon, and sulfur).

Energy Partitioning Schemes

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I shall give an overview, generalization, and systematization of the different energy decomposition schemes we have devised in the last few years by using both the 3D analysis (the atoms are represented by different parts of the physical space) and the Hilbert-space analysis in terms of the basis orbitals assigned to the individual atoms.

The so-called "atomic decomposition of identity" provides us the most general formalism for analyzing different physical quantities in terms of individual atoms or pairs of atoms. (The "atomic decomposition of identity" means that we present the identity operator as a sum of operators assigned to the individual atoms.) By proper definitions of the atomic operators, both Hilbert-space and the different 3D decomposition schemes can be treated on an equal footing.

Several different but closely related energy decomposition schemes have been proposed for the Hilbert space analysis. They differ by exact or approximate treatment of the three- and four-center integrals and by considering the kinetic energy as a part of the atomic Hamiltonian or as having genuine two-center components, too. (Also some finite basis correction terms may be treated in different manners.) The exact schemes are obtained by using the "atomic decomposition of identity". In the approximate schemes a projective integral approximation is also introduced, thus the energy components contain only one- and two-center integrals. The diatomic energy contributions have been also decomposed into terms of different physical nature (electrostatic, exchange etc.) The 3D analysis may be performed either in terms of disjunct atomic domains, as in the case of the AIM formalism, or by using the so called "fuzzy atoms" which do not have sharp boundaries but exhibit a continuous transition from one to another.

Energy decomposition in the DFT framework required introduction of a new concept, the "bond order density"; this quantity integrates to the bond order index of the given pair of atoms and corresponds to that part of electron density which may be considered responsible for the exchange effects corresponding to a given bond.

The different schemes give different numbers, but each is capable to reflect the most important intramolecular interactions as well as the secondary ones – *e.g.*, intramolecular interactions of type C-H...O.

Recent Advances in State-Specific Multi-Reference Coupled Cluster Formalism

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An overview will be presented in this talk of a suite of state-specific multi-reference coupled cluster (SS-MRCC) formalisms developed recently. They proved to be very successful in avoiding intruders via a rigorously size-extensive formulation, utilizing the MRCC ansatz of Jeziorski and Monkhorst but targeting only the desired state, rather than a group of states as is done in the state-universal (SU-MRCC) formalism. In the first formulation, the SS-MRCC formalism has more cluster amplitudes than the corresponding number of the virtual functions which form the complement to the model functions in the Hilbert space. This redundancy is exploited to ensure both size-extensivity and avoidance of intruders. Advantages and limitations of this formalism will be pointed out. An alternative approach, which obviates the need of invoking sufficiency conditions to ensure extensivity will be discussed next where the SSMRCC formalism will be shown to be mapped exactly into a dressed CI-like matrix eigenvalue problem which spans just the linearly independent Hilbert space in a given orbital basis. We will explore explicitly how a singles and doubles truncation scheme of cluster amplitudes in this formalism leads to a dressed MR-SDCI which produces manifestly size-extensive and size-consistent eigenvalues. We will also demonstrate how the eigenvalue equation-like structure of the working equations leads naturally to a more robust computational scheme not only for avoiding intruders but also for homing in to a desired eigenvalue. Implications of utilizing just the proper Hilbert space will be discussed, in particular in relation to a linear response version of the formalism for excitation or ionization energies in a strongly quasi-degenerate situation.

MP2 Energy and Gradient Calculations

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Density functional theory (DFT) is widely used to execute electronic structure calculations on large molecules as well as small molecules because of its low computational cost. However, the generally used DFT methods fail to describe non-covalent interactions that play a significant role in host-guest molecules, self-assembly, molecular recognition, and they usually underestimate reaction barriers. Many attempts have been made to develop new functionals and add empirical or semiempirical correlation terms to standard DFT but it seems that no widely accepted method has emerged yet. Second-order Moller-Plesset perturbation theory (MP2) is the simplest ab initio method that includes electron correlation effects important for non-covalent interactions and reaction barriers. MP2 is also helpful for checking DFT results. Despite these advantages, the formal scaling of MP2 energy calculations is fifth order, $O(N^5)$ (N is the number of basis functions), considerably higher than that of DFT energy calculations. In addition, much larger sizes of fast memory and hard disk are required in MP2 energy calculations. These make MP2 energy calculations difficult for large molecules. Recently, we have reported an efficient parallel algorithm of MP2 energy calculations, which is based on two-step parallelization and dynamic load balancing [1]. Besides energies, analytical energy gradients are essential for studies of molecular properties and structures. For this reason, a parallel algorithm of MP2 energy gradient calculations has been developed [2]. The high parallel efficiency of the developed programs makes MP2 energy and gradient calculations feasible for considerably large molecules and will enrich the important applications, especially to molecular systems where DFT is inferior to MP2 in accuracy and reliability.

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Ab Initio Rovibrational Spectrum of BeH_2^{2+}

Using IC-MRCI Property Surfaces

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An IC-MRCI ansatz has been used in conjunction with the beryllium [9s,8p,6d,4f,2g] [1,2] and hydrogen aug-cc-pVQZ [3] basis sets in order to construct an 89-point potential energy surface of the ground state of BeH_2^{2+} . The equilibrium structure was of C_{2v} symmetry, yielding a minimum energy of $-14.91607551 E_h$. A rational Padé analytical function was used to represent the discrete IC-MRCI grid. It was embedded in the t-coordinate Eckart–Watson Hamiltonian [4] in order to calculate vibrational and rovibrational wave functions. The analytical potential function possessed a square root of the residual error of 6.04 cm^{-1} relative to the discrete IC-MRCI energy grid. For the vibrational ground state, the vibrationally averaged bond lengths and angle of BeH_2^{2+} were 2.939 \AA and 30.3 degrees, respectively. Rovibrational radiative properties have also been calculated, employing an embedded analytical IC-MRCI dipole moment surface, transformed to the space fixed frame.

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MP2-R12 Versus Dual Basis MP2 Theory

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Explicitly correlated R12 approaches, based on the idea of Kutzeligg [1], have been intensively investigated during the last fifteen years, and, in particular at the MP2 level, they became accessible for large scale calculations [2-4]. The main goal is to recover for the basis set incompleteness error. The former formulation within the so called “standard approximation” (SA) [5] was more or less free from any ambiguities, however, in order to fulfill the SA requirements the calculations had to be limited to fairly saturated computational basis sets. A breakthrough came with the use of an auxiliary basis set for the resolution of identity [6]. However, introducing the auxiliary basis also implies diverse possibilities for formulating the problem, including the issue of the Hamiltonian splitting. In our contribution we have focused to that point. We compare results for possible Hamiltonian splitting, stressing the role of one-electron perturbation. We followed the matrix elements formulation as described recently [7].

A different possibility of recovering the basis set incompleteness error is offered by using the dual basis [8, 9]. The latter approach is confronted with MP2-R12, both concerning the computational demands and accuracy of the results.

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How Peter Pulay Helped Me Become An Applied Quantum Chemist

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Folding a protein into its native conformation results in a large range of chemical shift non-equivalence, with shift ranges of ~10 ppm being found for carbon-13 and ~35 ppm for nitrogen-15. The origins of these folding-induced shifts - which are essential for structure determination - were a mystery for over 20 years, but use of Pulay's Texas 90 program enabled their first successful prediction (de Dios et al. *Science*, 260, 1491-1496 (1993)). More recently, we have investigated the contributions to shielding in all 20 amino-acids, we have extended these results to paramagnetic systems (where shifts of ~5000 ppm are encountered), and combined the use of NMR, ESR and Mössbauer spectroscopy (isomer shifts and quadrupole splittings) with quantum chemistry to probe metal binding sites in protein, clarifying in several cases previous structural pictures (from x-ray diffraction). Updates in all areas will be provided in the talk.

Second Generation Car–Parrinello Method

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We present a new method for performing molecular dynamics simulations in which the forces are evaluated on the fly from electronic structure calculations. The method successfully unifies Car-Parrinello and Born-Oppenheimer approaches leading to a gain in computational efficiency of one to two orders of magnitudes depending on the system. High accuracy is maintained throughout irrespective of system size and band gap. A number of applications will also be presented.

Large Coupled Cluster Calculations on Inexpensive Parallel Computers: Applications to Weak Interactions

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A new parallel Coupled Cluster program (including related electron correlation methods such as Quadratic CI, CEPA-2, MP4) is described. The method uses Array Files [1] for message-passing parallelization, and is intended to be used on PC-based parallel computers. Spin adaptation is based on the Generator State formalism [2,3]. The program allows calculations of unprecedented size (e.g. over 1500 basis functions for QCISD) on inexpensive PC clusters. We have recently implemented triple substitutions. The new program has allowed us to get definitive results, e.g. for the benzene-benzene interaction, and for the interaction between aromatic molecules and water. Calculations on the interaction of aromatic surfaces and dihydrogen, an important problem in view of the potential use of carbon nanotubes for hydrogen storage, are also in progress.

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Recent Results in Molecular Quantum Chemical Kinetics from Spectroscopy: Symmetry Conservation and Beyond

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Peter Pulay's quantum chemical research has been crucial for relating results in molecular spectroscopy with accurate ab initio theory in the framework of the parity conserving quantum mechanics. Indeed, approximate parity conservation and conservation of nuclear spin symmetry are crucial concepts both in spectroscopy and reaction dynamics [1]. In our more recent research we have attempted to go beyond this in a fundamental way. Indeed, parity conservation would result in an exact equivalence of the spectra of the "mirror image" enantiomers of chiral molecules. However, electroweak theory in the framework of the "Standard Model" of modern high energy physics includes parity violation as an essential ingredient and predicts that the ground state energies of enantiomers of chiral molecules differ by a small "parity violating energy difference" ΔE_{pV} . A striking recent development was the discovery that improved theory predicts this energy difference to be one to two orders of magnitude larger than anticipated on the basis of older theories [2, 3, 4]. For CHFCIBr [5] ΔE_{pV} is now calculated to be about $10\text{--}11 \text{ J mol}^{-1}$ ($10\text{--}12 \text{ cm}^{-1}$) [6]. Such small energy differences can be measured following a spectroscopic scheme proposed in 1980/86 [7]. However, most of the spectroscopic ground work to even attempt such experiments was missing at that time. The Zurich group has since then undertaken efforts towards high resolution spectroscopy of chiral molecules with the goal of measuring ΔE_{pV} , but also to understand tunneling stereomutation in axially chiral molecules [8, 9, 10], new electroweak isotope effects [11], and femtosecond intramolecular vibrational redistribution as derived from high resolution spectroscopy of chiral molecules [12, 13]. In the lecture we will summarize the current status of these and related efforts. If time permits, we shall address also possible tests of CPT violation using chiral molecules [14, 15].

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Transition-Metal-Free Hydrogenation

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Catalytic hydrogenation is an important chemical reaction in a wide variety of areas, such as industrial processes, organic synthesis, and biological sciences. Most of these reactions are catalysed by transition metal complexes. For instance, compounds that contain platinum-group metals have been used extensively in the hydrogenation of fats in the food industry. In microorganisms, catalytic hydrogenation is carried out by enzymes known as hydrogenases. Most hydrogenases are metalloenzymes that contain nickel and/or iron-sulfur clusters. In contrast to transition-metal-catalysed hydrogenations, catalytic hydrogenation without transition metals is much less prominent. Among such studies, it has been found that strong acids can be used as catalysts for the hydrogenation of unsaturated hydrocarbons with molecular hydrogen. It has also been demonstrated that zeolites catalyse the hydrogenation of alkenes. Furthermore, it has been observed that some carbonyl compounds undergo catalytic hydrogenation in the presence of a strong base. In recent years, we have been interested in pursuing the fundamentals of transition-metal-free hydrogenation [1-7]. In this presentation, I will describe the findings of some of our recent studies in this area, including situations where kinetics does not follow thermodynamics.

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Modeling Reactions in Solution: Importance and Complexity

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The first part of this talk will motivate the need for modeling reactions in solution from our studies on free radical scavenging of NO by melatonin in water, and organocatalytic ring opening polymerisation of L-lactide in dichloromethane. The second part will then consider the issues that arise with a localised basis QM/MM approach, allowing for explicit solute-solvent interactions within the framework of periodic boundary conditions, and use of Ewald formalism for proper treatment of long-range effects.

**Nuclear Dynamics in Degenerate Electronic States:
Spectroscopy and ab Initio Calculations for Pseudorotating B_3 and C_3^+**

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Electronic degeneracy usually implies strong rovibronic coupling on flat potential surfaces with large-amplitude motions. Understanding of these motions and assignment of the resulting irregular spectra requires accurate electronic structure calculations and variational treatment of the nuclear motion taking proper account of the geometric phase boundary conditions. Electronic E-state degeneracy is encountered in excited states of B_3 , which have been observed in matrix absorption spectra, and in the ground state of C_3^+ which is an important intermediate in astrophysically relevant reaction chains. The Jahn-Teller effects and the use of hyperspherical coordinates will be described (with reference to previous work on Li_3 and Na_3 by Demtröder and Meyer). Emphasis is given to the discussion of characteristic features of vibrational wave functions and energy levels.

Estimating Virtual Quantities: Aromaticity, Strain, Conjugation, Hyperconjugation, and Branching

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The energies associated with many highly useful chemical concepts, *e.g.*, “aromaticity,” are not directly measurable experimentally. Traditional evaluations of such virtual quantities require comparisons with arbitrarily chosen reference models. The conventional selections suffer from “contaminating” effects (other than the one under consideration). Consequently, widely accepted quantitative numerical values for, *e.g.*, conjugation, hyperconjugation, aromaticity, etc. are underestimated considerably [1-3]. Molecular quantum mechanics not only permits a far greater choice of reference models but also facilitates detailed analysis. The title subject is reexamined critically. Substantially revised estimates are recommended. Reasons for preferring isodesmic bond separation energy (BSE) evaluations over those involving homodesmotic equations are put forward. Conceptual advances provide new insights. Net attractive 1,3-alkyl-alkyl interactions, which are responsible for the greater stability of branched hydrocarbons, also are present in *n*-alkanes. Hence, the latter are compromised as reference molecules. This has major consequences for many energy evaluations. Thus, if based on propane and ethane, the “strain energy” of cyclopropane is overestimated by nearly a factor of two compared to the BSE value, based on methane and ethane [3].

The Block Localized Wavefunction (BLW) method, which combines the advantages of VB and MO theory, provides evaluations based on the Pauling–Wheland definition of „resonance energy” [2] (the energy difference between the system of interest and the BLW-derived hypothetical chief resonance contributor). In effect, π -type interactions can be „turned off” selectively. The influences of, *e.g.*, hybridization and strain, are preserved. The implications of many BLW applications to the energies associated with conjugation, hyperconjugation, aromaticity, antiaromaticity [2,3] and other interactions in intriguing systems will be discussed.

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Hybrid Functionals for Solid-State Systems

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This presentation will address our current efforts to develop more accurate exchange-correlation functionals for Density Functional Theory. One of the functionals to be discussed is a screened Coulomb potential exchange hybrid called **HSE** [1], which is particularly well suited for calculations of solids because it is much faster than regular hybrids and can also be used in metals and systems with negligible band gaps. **HSE** yields an important improvement in band gap estimates [2] compared to **LDA**, **GGAs**, and meta-**GGAs**. We will also present applications to transition metal oxides, silicon phase transitions and defects [3], and other problems where electron localization seems to play a crucial role [4].

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Exploring Potential Energy Surfaces with ab Initio Molecular Dynamics

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For the reaction of formaldehyde radical anion with methyl chloride, one transition state leads to two different products. Since the bifurcation in the reaction path occurs after the transition state, molecular dynamics is needed to study the branching ratio. Bond additivity corrections are used to improve the potential energy surface for the ab initio molecular dynamics study. Another reaction in which the branching ratio has been explored by ab initio molecular dynamics is the keto-enol isomerization and dissociation of acetone radical cation. Dynamics favors the dissociation of the newly formed methyl group, in agreement with experiment. For molecules subject to short, intense laser pulses, the dynamics of the electrons rather than the dynamics of the nuclei dominate the initial response. The behavior of polyenes and polyacenes subject to intense fields is modeled by integrating the time-dependent Hartree-Fock equations. Short, intense infrared pulses are found to produce non-adiabatic electronic excitations.

Hybrid and Macroconfiguration Coupled-Cluster Methods

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Coupled-cluster theory through perturbative triple excitations, CCSD(T), has become a “gold standard” of electronic structure theory, providing very high-accuracy results in many cases. However, there remain challenging problems which lie beyond the reach of CCSD(T), either because of the method’s unfavorable computational scaling with system size, or because electronic near-degeneracies become large enough to cause a breakdown in the CCSD(T) approximation. Active space concepts may be applied to coupled-cluster theory to minimize the number of higher-order terms required in challenging applications. Hybrid methods which treat most terms with inexpensive perturbation theory (*e.g.*, MP2) and a few important (active space) terms more completely with coupled-cluster theory (*e.g.*, CCSD) suffice to provide semiquantitative results for simple bond-breaking reactions, whereas standard RHF MP2 diverges in these cases. In more difficult bond-breaking reactions such as those breaking double bonds, only a few higher-order excitations are typically important, and they can be efficiently included using “macroconfigurations” of electron distributions, in a generalization of the restricted or general active space concepts. These approaches have been implemented within the context of a general-order, active-space coupled-cluster code built on top of our efficient string-based determinant CI program.

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NO₃: The Molecule Without a Structure

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Spectral lines associated with the NO₃ molecule were first detected and reported by Chappuis in the period 1880-1882. Although the carrier of these lines was not determined without ambiguity, it still remains a fact that this may well have represented the first spectroscopic detection of a polyatomic radical. In the intervening century and a quarter, NO₃ has emerged as both an important species in the nighttime atmosphere as well as a major challenge for molecular spectroscopy. The difficulties in the spectroscopy lay in the exceedingly complex quantum mechanics that governs the molecule; there are five low-lying electronic states, and vibronic interactions mixing these states are ubiquitous. This talk focuses on the ground electronic state of NO₃, which is strongly coupled (*via* a pseudo-Jahn-Teller interaction) with an excited state having ²E' symmetry that is positioned roughly 2 eV higher in energy. Through use of a model Hamiltonian approach, the identity of most vibronic levels within 3000 cm⁻¹ of the zero-point level is revealed, and a number of spectroscopic misassignments are corrected and other unassigned lines are properly accounted for. The question the molecular structure of NO₃ is discussed towards the end of the talk, where it will be argued that viewing the molecule as a symmetric *D*_{3h} species is appropriate to understand its spectroscopy, while viewing it as a *C*_{2v} species effectively rationalizes its remarkably high reactivity. The question of the symmetry associated with the minimum on the adiabatic potential energy surface is largely irrelevant in this regard.

Protein Folding Studied by Computer Simulation on Blue Gene at IBM

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IBM began the Blue Gene project in 2000 to build a massively parallel supercomputer and use it to study important biophysical processes, including protein folding. This project has produced some of the most powerful computers in the world, one of which is used inside IBM's Research Division to study protein folding. This talk will describe some of that research effort. The focus will be on a two-year study of the thermodynamics and kinetics of folding of an 80 amino acid protein construct known as lambda repressor [λ lambda(6-85)]. Minor mutations of this protein have produced some of the fastest folders known, and the time scales accessible in folding simulations are beginning to meet the folding times observed in experiments. Our simulations reveal a complex, hierarchical folding process, with different structural elements forming at different temperatures. This talk will also address some of the challenges inherent in studying protein folding by simulation, including the very wide temporal dynamic range, and some of the limitations of classical force fields.

In order to perform their biological function, most proteins need to fold into well defined, complex three dimensional conformations. In fact, the proteins in living organisms have evolved not only to perform their specific functions, but to be "foldable," *i.e.*, able fold into the required conformations quickly enough to be biologically useful. These folded structures are stabilized by hydrophobic interactions, weak electrostatic interactions, and hydrogen bonding both within the protein as well as with solvent. For some proteins the folding process is aided by interactions with other molecules, chaperones, but there are a large number that can fold and unfold reversibly without assistance when denatured thermally or chemically. For this class of proteins, the final structure as well as the mechanism and rate of folding are effectively encoded in the amino acid sequence.

Understanding protein folding has a number of important applications. First, there are a large number of folding related diseases, including many genetic diseases where a gene mutation has caused an amino acid substitution, deletion or insertion that affects the final structure of the protein or the rate at which it forms. A thorough understanding of the folding process could suggest ways to intervene in these diseases. Second, a good understanding of protein folding principles would allow us to exploit them in industrially important areas of nanotechnology.

Fully Variational Hartree–Fock Computations on Atoms and Molecules

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The Hartree–Fock–Roothaan–Hall self-consistent-field theory [1-5] still occupies the central point of wave-function-based electronic structure theory [6]. The ingenious introduction of Gaussian-type basis functions (GTF) by Boys [7] determined most of the developments of ab initio quantum chemistry techniques, including energy and derivative computations [8]. To compensate for the wrong functional behavior of GTFs both near and far from the nuclei, it is typical to use a substantial number of them in accurate electronic structure computations. However, instead of using lots of atom- and bond-centered GTFs of increasing complexity, there is another possibility to make the basis set truly flexible: the GTFs can be allowed to fully relax during the electronic structure computation, both with respect to their distribution and exponents [9]. Fully variational energies and structures have been obtained for the few-electron prototypical atomic and molecular systems H_2^+ , H_2 , HHe^+ , H_3^+ , Be , LiH , BeH , BH , and CH at the Hartree–Fock (HF) basis set limit (HFL). The HFL computations are made possible by a global optimization technique [10] based on analytic gradient vector of the total energy. The efficiency of the procedure presented means that the HFL structure and energy of few-electron systems can be obtained with a few dozen distributed *s*-type GTFs. The availability of HFL results along a potential energy curve allows the investigation of the relative accuracy of traditional HF computations utilizing correlation-consistent basis sets [11] and extrapolation procedures [12,13]. The direct energies are very accurate and the extrapolated ones are nearly exact close to the equilibrium structure and close to complete separation of the atoms, but at moderate and short distances the accuracy drops substantially and systematically. This behavior should be kept in mind when traditional HF computations are used as energy components to obtain global potential energy surfaces.

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Efficient Explicitly Correlated R12 Methods Using Gaussian Geminals

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Explicitly correlated wave function methods offer much smaller basis set error than their standard counterparts primarily due to the efficient description of the Coulomb hole. Explicitly correlated R12 methods [1,2] are currently the most practical such approaches due to the clever use of the resolution of the identity (RI) and other approximations to avoid many-body integrals. Recent marriage of the Gaussian geminals methods with the R12 technology [3] seems a promising approach to the general Coulomb correlation problem. R12 (or F12) methods using as few as 3 Gaussian geminals have been recently shown capable of better than 98% precision for correlation energy using only a double-zeta basis set, without any approximations other than RI. Such precision is comparable to that of a sextuple-zeta conventional calculation, but obtained at a much lower computational cost. Here I will review representative performance of R12 Gaussian geminals methods for thermochemical properties, explore technical simplifications, and offer an outlook for more compact and efficient explicitly correlated ansatze.

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Exploring Electronic Structure with Constrained Density Functional Theory

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We show that several of the major shortcomings of approximate density functionals can be overcome by applying physically motivated constraints to the electron density. We summarize our implementation of this constrained density functional theory (CDFT) and present several illustrative applications that demonstrate the strengths of the new formalism: 1) CDFT allows charge transfer excitations to be treated accurately within a ground state formalism, including the long range $-1/r$ interaction between the electron and the hole 2) Low-lying spin states and exchange couplings can be obtained without artificial symmetry-breaking 3) One can properly dissociate both one- and two-electron bonds and accurately predict certain barrier heights by performing a small configuration interaction calculation in the basis spanned by the constrained states. Thus, it appears that constraints offer the possibility of significantly expanding the range of problems accessible using DFT.

The Effect of Local Approximations on the Calculation of Molecular Properties and Reaction Energies

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The current status of local correlation methods, as originally proposed by Pulay, is reviewed. The influence of the local approximations on the accuracy of calculated reaction energies, dipole moments, polarisabilities, as well as harmonic and anharmonic vibrational frequencies is studied using canonical and local MP2, CCSD, and CCSD(T) methods. The effects of the basis set size, the domain sizes, and the weak pair approximations on these properties is systematically investigated. For medium size basis sets (aug-cc-pVTZ) the deviations between the results of standard local calculations canonical calculations are smaller than basis set errors. For larger basis sets it is necessary to increase the domains and the list of strong pairs to keep the balance between basis set errors and local errors. This can be achieved by the adjustment of a single parameter, which allows to approach the canonical results systematically to any desired precision. We discuss strategies how to approach the complete basis set limit of CCSD(T) at minimal cost using local methods.

Geometry Optimization and Vibrational Harmonic Frequency Calculations with a Dual Basis Set Approach

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One of the most important tasks in modern quantum chemistry is to extend applicability of computational methods to larger and larger molecular systems. This can be achieved only by reducing numerical cost of these calculations. Less expensive methods together with the newest computer science technology and methodology, like parallel computing, make it possible.

In the majority of the quantum chemical methods the most time consuming step involves calculations and handling of the electron-electron repulsion integrals. It is true not only for the HF or DFT methods but also for post-SCF methods like MP2. Computational cost of the SCF (HF and DFT) and MP2 methods increases very quickly with a molecular size N (number of basis functions or atoms). Formally, these methods scale as N^4 and N^5 , respectively.

A lot of effort has been made last years in order to reduce computational cost of the quantum chemistry methods with controlled loss of accuracy. First of all, efficient procedures for selection of small, *i.e.*, unimportant two-electron integrals have been proposed. Such integrals do not have to be calculated. An efficient two-electron integral prescreening reduces computational cost in the SCF methods to about $N^2 \cdot N^3$ [1]. Further savings have been obtained by using fast numerical techniques, called linear scaling methods. Among those, the fast multipole [2], resolution of identity or density fitting [3] and pseudospectral [4] methods seem to be very successful. These methods as well as methods based on the plane waves [5] like Fourier Transformed Coulomb [6] eliminate necessity of calculating most of the classical Coulomb two-electron integrals. Some of these methods can be applied also at the MP2 level. Here, the use of localized orbitals (instead of canonical) as suggested by Pulay [7] has been very successful (LMP2). It should be emphasized that calculations of the MP2 correlation energy for larger molecules are now less expensive than the preceding SCF step.

At this point the issue of the basis set should be addressed. In practice, computational cost of linear scaling methods increases with molecular size nearly linearly only with relatively small basis sets, *i.e.*, at most the polarized double- ζ type [8]. With larger basis sets the molecular size scaling of these methods is much higher, mostly because the overlap matrix loses its sparsity. On the other hand, larger than polarized double- ζ basis sets are required in order to achieve high accuracy results, *i.e.*, close to the complete basis set limit. For typical molecules this is approached with roughly 6-311++G-(3df,3pd) type of a basis set in SCF methods. Using such a basis set for larger molecular systems results in a very high computational cost. Situation is even worse in the case of electron correlation calculations where convergence toward the basis set limit is much slower. Accurate description of dynamical electron correlation requires orbitals with many angular and radial nodes, *i.e.*, higher angular momentum functions. Such functions are necessary for correct representation of virtual orbitals. It should be pointed out that such functions do not contribute significantly to the occupied orbitals and therefore they are not really needed in the preceding SCF calculations. This was first realized by Jurgens-Lutovski and Almlöf [9] in MP2 calculations. These authors proposed to use a relatively small basis set for the SCF step in order to obtain occupied orbitals and then an extended basis to describe virtuals for correlation calculations. At the SCF level this idea of *dual basis sets* was first introduced by Havriliak and King [10] for Rydberg states.

Following Almlöf's work, we have recently implemented the dual bases set approach within the MP2 method in the PQS program package [11]. In this dual basis MP2 method (DMP2) the SCF calculations are performed in a small basis set yielding converged solutions of the HF equation. It is assumed that small basis set was good enough to describe occupied orbitals accurately. Then an extended basis set is introduced (it is convenient to use such a combination of small and large basis sets, that a small one is a subset of large one). Small basis set density (**d**) is projected into that large basis set (**D**) and used to construct the Fock matrix **F(D)**. This Fock matrix is a source of new eigenvectors and eigenvalues in a large basis set. Last year, Steele *et al.* [12] proposed to use in DMP2 all (occupied and virtual) orbitals and energies obtained from diagonalization of the **F(D)**. Since direct

diagonalization of the $\mathbf{F}(\mathbf{D})$ matrix would mix extension basis functions in occupied orbitals, we diagonalize rather the projected (against occupied space) Fock matrix, $\mathbf{F}^{\text{vir}} = (1 - 1/2\mathbf{SD})\mathbf{F}(1 - 1/2\mathbf{DS})$. Thus, in our method, the occupied space is given by the converged, small basis SCF, while virtual orbitals and energies are obtained via diagonalization of the \mathbf{F}^{vir} matrix. The same choice of eigenvectors and eigenvalues in a large basis set was also used last year by Nakajima and Hirao [13]. Regardless of the particular choice of the occupied and virtual space, the whole procedure is equivalent to a single Roothaan step, *i.e.*, one SCF iteration in a large basis set starting from a small basis set guess.

Correlation energies $\varepsilon_{\text{DMP2}}$ obtained with the DMP2 method remain very close to the full large basis set MP2 values ε_{MP2} . However, the total energy obtained with a dual basis set ($E_{\text{scf}} + \varepsilon_{\text{DMP2}}$) and with a large basis set ($E_{\text{SCF}} + \varepsilon_{\text{MP2}}$) differ significantly because, an extended basis set SCF yields of course lower E_{SCF} energy than small basis set E_{scf} . We have proposed to correct a small SCF energy E_{scf} with respect to the basis set extension to the larger one. Since in a single SCF iteration with a large basis set the convergence is not reached, the Brillouin theorem is not satisfied leaving occupied-virtual block in the MO Fock matrix non-zero. We used these matrix elements as a perturbation and calculated the second-order energy correction as

$$\Delta E_{\text{scf/SCF}} = E^{(2)} = 2 \sum F_{ia}^2 / (e_i - e_a) \quad (1)$$

where i and a denote occupied and virtual orbitals, respectively. A small basis SCF energy with this correction

$$E_{\text{DSCF}} = E_{\text{scf}} - \Delta E_{\text{scf/SCF}} \quad (2)$$

(dual basis SCF) approximates the large basis SCF energy ESCF very well, within a few microhartrees. An alternative way of correcting a small basis set SCF energy was suggested last year in ref [12]. Those authors calculate energy lowering using changes in density matrix due to a single Roothaan step

$$\Delta E_{\text{scf/SCF}} = \text{Tr}[(\mathbf{D}' - \mathbf{D})\mathbf{F}(\mathbf{D})] \quad (3)$$

where new density \mathbf{D}' is obtained from diagonalization of $\mathbf{F}(\mathbf{D})$.

With a reasonable and appropriate choice of small and large basis sets, the dual basis set MP2 energy

$$E_{\text{DMP2}} = E_{\text{DSCF}} + \varepsilon_{\text{DMP2}} \quad (4)$$

gives a very good approximation to the full, large basis set value

$$E_{\text{MP2}} = E_{\text{SCF}} + \varepsilon_{\text{MP2}} \quad (5)$$

Accuracy of relative energies is even better [11]. With dual basis set MP2 high accurate results are obtained at a significantly lower computational cost as compared to the traditional, large basis set MP2.

The saving here is twofold. For the MP2 correlation energy, two-electron MO integrals ($ia|jb$) are needed where occupied orbitals i, j are represented only in a small basis set. Thus, for MP2 we need to calculate only $(\mu\nu|\chi\sigma)$ AO integrals with μ, χ belonging to a large and ν, σ to a small basis set. If dimensions of large and small basis sets are N and n then, the number of integrals is reduced from N^4 to N^2n^2 .

The saving is even more pronounced at the SCF level. The SCF step with a small basis set should be $(N/n)^4$ times faster than with a large one. An additional cost arises from a single build of the large-basis Fock matrix needed for the $\Delta E_{\text{scf/SCF}}$ correction and virtual subspace. This is less expensive than one large-basis SCF iteration because an aggressive integral screening can be applied [11,12]. The overall saving obtained with the dual basis set MP2 method is often more than an order of magnitude as compared to the large basis MP2.

With the energy correction (1) or (3), the dual basis set approach may be used also at the SCF level. Recently, two such papers have been published with the dual basis sets used in the DFT method [14,13]. The results presented there for absolute energies and atomization energies [HG] for 56 molecules showed that the dual basis DFT method can be very successful. Also the dual-basis DFT

spectroscopic constants (bond lengths and harmonic frequencies calculated by 5-point energy fitting) for first-row diatomic molecules agreed well with larger basis set DFT [13].

High accuracy and significant saving offered by the dual basis set approach in energy calculations makes it potentially attractive technique for geometry optimization. The first paper with analytic gradient of dual basis HF and DFT energies was published last year by Steele *et al.* [15]. Calculations of the gradient of the dual basis SCF energy (2) with energy correction (3) require a solution of the coupled-perturbed equations. Even so, the saving reported in [15] for nuclear forces calculations was up to 75% compared to large basis calculations.

In this study we explore performance of the dual basis set HF and MP2 methods in calculations of the first- and second derivatives of energy with respect to the nuclear positions. These derivatives were calculated numerically. Geometry optimization with dual basis sets at the HF and MP2 levels have been performed for a set of 50 molecules. For somewhat smaller set of molecules vibrational harmonic frequencies have been calculated. We will present results obtained with two versions of the dual basis approach as originally proposed by us in [11] and by Steele *et al.* in [12].

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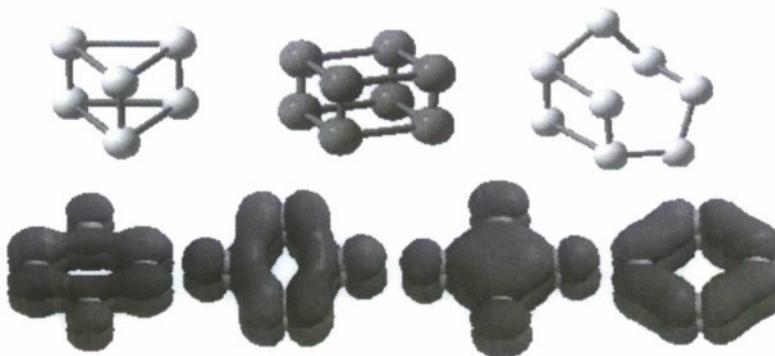
$\pi^*-\pi^*$ Interaction in Sulfur and Oxygen Chemistry

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A novel type of chemical force, $\pi^*-\pi^*$ interaction, is essential to understand the molecular geometries of many sulfur- and oxygen-containing compounds, including the prism structure of S₆ [1], spiral cluster and cuboid structures of S₈ [2], and singlet open-chain isomers of S₇ [3], branched rings of binary sulfur oxides SnO₂ [4-6]. The unusual molecular geometries can be understood in terms of the $\pi^*-\pi^*$ interaction between the π^* orbitals of the two S=S (or S=O) moieties. The nature of chemical bonding in these sulfur and oxygen-containing compounds is probed by charge density analysis based on quantum theory of atoms in molecules. Remarkably, well-defined rhomboid O₈ (D_{2h}) molecules have been observed very recently in dark-red ϵ -O₂ phase of solid oxygen [7]. *Ab initio* calculations [8] have assisted in the further characterization and understanding of this surprising molecule. Again, the concept of $\pi^*-\pi^*$ bonding between open-shell species can explain the formation of O₈.



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Time-Dependent Density Functional Theory As a Practical Tool in the Study if MCD and CD Spectra of Transition Metal Complexes. Implementations and Applications

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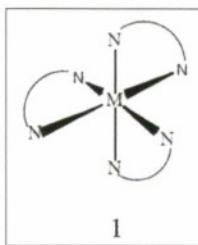
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We have recently implemented methods for the calculation of electronic¹ and magnetic circular dichroism² based on time-dependent density functional theory (TD-DFT). We report here applications of the method to transition metal complexes. The first part will discuss the CD-spectrum of the classical M(L)₃ complexes where L is a bidentate ligand, **1**. The origin of the optical activity as revealed by TD-DFT will be compared with classical interpretations based on crystal field theory and the Kirkwood polarisability model. The second part concentrates on the calculation of the A,B and C terms in the MCD spectra of transition metal complexes. We discuss finally possible biological applications, **2**. Comments will also be given about the complications added to TD-DFT when dealing with open shell transition metal complexes.



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SESSION CHAIRS

The Implications of the Pseudo-Jahn-Teller Model in the Bending of the MY_2 Molecules (M=Ca, Sr, Ba; Y=F, Cl, Br)

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It is well known that most common models (VSEPR, Walsh diagrams, ionic models, etc.) for the linear MY_2 molecules shown in the title predict them to be linear. However, the lower the metal and the higher the ligand are in the periodic table the more probable the resulting molecule is bent. Several models have been proposed to explain these deviations including the effect of polarization in the metal [1], the position of the band associated with the excitation of a d-electron [2], rationalization of the problem through LCAO diagrams and ab initio calculations [3] and the tetrahedral distortion of the electronic core of the metal as studied by the theory of atoms-in-molecules [4]. Even though the previous models are disparate in their conclusions most agree in the importance of the d-shell of the metal in the distortion.

We have carried out *ab initio* calculations of the ground state energy surface at various levels (HF, MP2, CISD, B3LYP, CASSCF, CASPT2) and that of the several excited states using CAS and CASPT2 and interpreted them using pseudo Jahn-Teller theory. We clearly show that the origin of the distortion is due to the mixing of the ground electronic state with the lowest excited one, which depends on the excitation energy from the d-shell of the metal. As the result of this mixing the electronic density around the metal is tetrahedrally distorted and we are able to unify all previous explanations into a single theory.

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[P-2]

Bond-Stretched Invertomers

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A bond-stretched invertomer is the less stable of two bond-stretch isomers which differ by the inversion of two atoms. Some examples of molecules that have bond-stretched invertomers are hexafluorocyclopropane and trisilacyclop propane. The conditions necessary for the existence of a bond-stretched invertomer as a potential energy minimum are strong through-space or through-bond interactions between two radical centers and large barriers to inversion of these centers. The possible role of the bond-stretched invertomer of hexafluorocyclopropane as a new type of reactive intermediate in the halogenation reactions of its lower energy isomer will be discussed.

Embedded Configuration Interaction Theory for Metallic Systems: From Kondo Physics to Chemisorption

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We will present our latest advances and applications of an embedding theory that addresses shortfalls of standard implementations of density functional theory (DFT), the origins of which are incomplete knowledge of the exact exchange-correlation functional. We embed a correlated quantum chemistry description into crystalline surroundings described by periodic DFT [1]. Recent technical advances in the theory include: (i) implementation of ultrasoft pseudopotentials (USPPs) in a consistent manner across all levels of theory (periodic DFT, CASSCF, and C1), (ii) self-consistent updates of the density of the total system, thereby allowing a fully-self-consistent embedding operator, and (iii) a multi-reference singles and double excitation C1 (MRSDCI) treatment of electron correlation in the embedded region [2]. This embedded configuration interaction (ECI) theory is used to study a variety of systems/phenomena where DFT is known to fail, due to either neglect of many-body effects or self-interaction artifacts. We will illustrate how the embedding theory is able to give a *qualitatively (as well as quantitatively)* different view of these systems/phenomena. We apply ECI theory to the Kondo effect, a long standing problem in condensed matter physics. The Kondo effect refers to the observation of an anomalous resistivity minimum at low temperatures for materials containing magnetic transition metal impurities in nonmagnetic host metals. We show that the ECI theory is able to capture the physics and offer a new view of this phenomenon, while periodic DFT and finite cluster quantum chemistry calculations do not. We also apply ECI theory to the long-standing problem DFT has with chemisorption site preferences for CO on metal surfaces [3].

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Ab-initio DMRG and Canonical Transformation

Theories of Electronic Structure

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I will describe two complementary methods that are under development in our group: (1) Ab-initio Density Matrix Renormalization Group: The Density Matrix Renormalization Group (DMRG) is a natural multireference method. Recently, we have implemented a quadratic-scaling DMRG algorithm which opens up the description of multireference (strongly interacting) correlation in large quasi-one-dimensional systems [1]. I will report calculations using this technique on conjugated oligomers correlating exactly, in the sense of Full-CI, complete pi-active spaces with up to 100 electrons in 100 orbitals (100, 100). (2) Canonical Transformation Theory: We have been developing a canonical transformation method to incorporate dynamical correlation on top of a multireference starting point. Our theory, termed Canonical Transformation Theory (CT) [2] is based on a unitary exponential ansatz and is size-consistent. I will present a number of calculations using this method which demonstrate that it retains the accuracy of coupled cluster theory at equilibrium bond geometries, but extends this accuracy to the full potential energy surface. The formal computational scaling is the same as coupled cluster theory and observed timings are faster than CASPT2, while accuracies are competitive with MR-ACPF. I will also describe our initial efforts to develop a reduced-scaling version of the theory for large molecules.

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Molecular Dynamics Simulations of Natively Unfolded Nucleoporins

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The nuclear pore complex (NPC) gates all macromolecular exchange between the nucleus and cytoplasm of cells. Its transport conduit is populated by a family of NPC proteins, the nucleoporins (Nups) that feature natively-unfolded domains with multiply repeated phenylalanine-glycine motifs (FG nups). Although these proteins play key roles in nucleocytoplasmic transport, little is known about their properties and dynamics. We used classical molecular dynamics (MD) simulations to characterize the "dynamical structure" of a representative FG domain from the yeast GLFG nucleoporin Nup116 and a non-functional mutant in which all of the phenylalanines were replaced by alanines. For each Nup, we ran multiple replicates of 5 nanosecond MD trajectories and used various analyses to characterize the rapidly changing ensemble of configurations produced. These analyses were performed on structures sampled every 1 picosecond from the final 3 nanoseconds of simulation. Autocorrelation functions of the phi-psi angles and overall protein structure showed that the Nups continuously change configuration during the simulation period. Secondary structure analysis of the sampled configurations indicated that residues are in well-defined secondary structures only a small fraction of the time. Also, no significant difference in secondary structure content between wild type and mutant FG domains was detected. Calculation of two measures of protein compactness, the radius of gyration and the C- to N-terminal distance, show that at elevated temperatures (350K) the wild type domain adopts a more compact ensemble of structures than the mutant. To characterize the structures further we calculated inter-residue probability distribution functions between all pairs of phenylalanines (or substitute alanines) in the FG domain. Statistical analysis of these distributions shows a higher level of correlation between inter-residue distances in the wild type domain than the mutant.

The Current State of Ab Initio Calculations of Optical Rotation and Circular Dichroism Spectra

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We review the current state of the art in first-principles calculations of electronic chiroptical properties, including optical rotation angles and circular dichroism rotational strengths. Both rigid and conformationally flexible systems are considered, including substituted oxiranes and thiiranes, as well as substituted allenes, which are characterized by stereogenic axes rather than stereogenic centers. Comparison with both gas- and liquid-phase experimental data are given, particularly for problematic species such as norbornenone and the pinenes. In addition, we discuss recent developments in reduced-scaling/localized methods for extension of highly correlated linear response models to large molecules.

Do Chemical Reactions without a Transition State Possess a Distinctive Reaction Mechanism?

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Recombination reactions often proceed without a classical barrier. In the case of atom-atom reactions without barrier the electronic changes along the reaction path are mostly trivial and easy to determine. However, when larger labile molecules recombine it becomes often difficult to find out whether a TS does or does not exist and whether, in the latter case, the reaction proceeds with distinct mechanistic changes. We present a new method for detecting TSs on a potential energy surface (PES). The method is based on the search of a growing string (GS) along reaction pathways defined by different Newton trajectories (NT). Searches with the GS-NT method always make it possible to identify the TS region because monotonically increasing NTs cross at the TS or, if not monotonically increasing, possess turning points that are located in the TS region. In turn, it is also possible to positively exclude the existence of a TS thus identifying the reaction as truly barrierless. The GS-NT method is applied to quasi-barrierless and truly barrierless chemical reactions. For each of these reactions, a mechanistic analysis is represented, which reveals that barrierless reactions can possess distinct mechanisms leading from first van der Waals interactions to the actual chemical processes. It will be discussed when, under environmental impact, such barrierless reactions change their mechanism in such a way that a TS or even an intermediate and two TSs appear on the PES.

Direct Estimate of Conjugation, Hyperconjugation and Aromaticity with the EDA Method

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The concept of π electron delocalization via double bonds which are separated by one single bond is an important bonding model in chemistry. Conjugative interactions play a major role in explaining geometries and reactivities of unsaturated molecules particularly in organic chemistry. While the latter effects are observable quantities, π conjugation itself is a virtual quantity which cannot be measured directly. A special class of π conjugated species are aromatic compounds which exhibit a particular stability if the number of π electrons in the cyclic system follows the $4n + 2$ rule. Even saturated compounds may become stabilized by the interaction of π orbitals which is termed hyperconjugation. Numerous descriptors have been suggested in the past for estimating the strength of conjugation, hyperconjugation and aromaticity. In the context of analyzing the nature of the chemical bond using an energy decomposition analysis (EDA) [1] we found that the strength of the intrinsic π orbital interactions correlates very well with experimental quantities which have been suggested as indicators for π conjugation, such as Hammett constants and ^{13}C NMR chemical shifts. The EDA values for ΔE_{π} are very useful for directly estimating the strength of conjugation, hyperconjugation and aromaticity without using external reference values [2].

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Improved Double-Hybrid Density Functionals

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Non-local electron correlation effects are responsible for important parts of the interaction between atoms and molecules. An example are the dispersion (van der Waals) interactions that contribute significantly to many non-covalent bonds, especially in larger systems usually considered in the modern fields of bio-, supramolecular-, or nano-chemistry. We show results from new double-hybrid density functionals (X2PLYP)[1] that add a previously developed empirical dispersion term (DFT-D)[2] to the energy expression but leave the electronic part untouched. Results are presented for the S22 set of non-covalent bonding energies, the G3/99 set of heats of formations, and conformational energies of a phenylalanyl-glycyl-glycine peptide model. A significant increase in accuracy for non-covalent interactions as well as for thermochemical data is obtained. The proposed composite approach (X2PLYP-D) is of competitive accuracy to higher-level coupled-cluster energy calculations. The improvements obtained for the G3/99 set emphasizes the importance of intramolecular dispersion effects in large molecules. In order to further demonstrate the perspective of the new approach it is applied to several problems which are known to be challenging cases for common density functionals. In all cases, excellent agreement with reference data are obtained.

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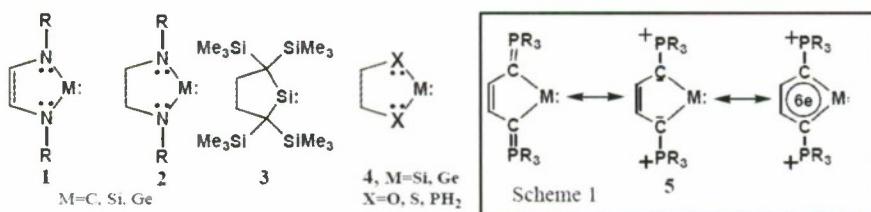
Novel, Potentially Stable, Heterocyclic Silylenes and Germynes. A Theoretical Study

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Silylenes and germynes, the heavier congeners of carbenes, were observables only at low temperatures. During the mid 1990s, N-heterocyclic carbenes, silylenes and germynes (e.g., 1 and 2) were reported.¹ These compounds are stable at room temperature under anaerobic conditions. They are stabilized both by the electronic effect of the amino groups and by steric protection maintained by their bulky substituents. The first stable alkyl silylene, 3, which is sterically protected, was reported in 1999 by Kira et al.¹

Here we report a computational study of the stability of heterocyclic silylenes and germynes **4** (X = O, S, and PH₂) and **5**, with the aim to locate a novel class of stable silylenes and germynes. Our study predicts that according to various thermodynamic and magnetic criteria **5** (M = Si and Ge) are as stable as the N-heterocyclic molecules **1** (M = Si, Ge). **5** benefits from an electronic stabilization which can be attributed to the possible resonance structures shown in scheme 1. Due to the possibility to substitute it with bulky substituents, **5** can be sterically protected, making it also stable kinetically, and a potential candidate for synthesis and isolation.



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Magic Structures and Quantum Conductance of Silver Nanowires and Design of Stable Linear Single Atom

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Based on first principles theory, we have investigated the nanowires [1-4]. Here, we discuss the thinning process of silver nanowires (NW) [5] and the design of stable linear single atomic chains with charge-transfer-driven alloying approach [6]. The pathway of thinning process for transient [110] NWs of Ag is elucidated. The result is in good agreement with experimental observations. An unambiguous identification of the structure of a NW requires at least two views along different directions. In the cases where two views of different NW structures are practically the same for very thin NWs which pose experimental difficulty due to small signal-to-noise ratio, our theoretical analysis helps distinguish these structures. From the conductance (G) calculations vis-a-vis the structure of transient NWs, the puzzling experimental observation of fractionally quantized G values are explained by considering the existence of mixed structures for thin wires. Then, on the basis of first principles calculations of clusters and one dimensional infinitely long subnanowires of the binary systems, we find that alkali-noble metal alloy wires show better linearity and better stability than either pure alkali metal wires or noble metal wires. The enhanced alternating charge build-up on atoms due to charge transfer helps the atoms line up straight. The cesium doped gold wires showing significant charge transfer from cesium to gold can be stabilized as linear or circular monoatomic chains.

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[P-12]

Self-Consistent Valence Pairs

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The complete active space MCSCF approach has been extraordinarily successful in providing a robust zero-order formulation for ground-state and low-lying excited-state electronic structure problems. Its principal defect is that its demand on computational resources grows in principle exponentially with system size; for practical applications this usually means that a difficult choice of a reduced set of active orbitals has to be made.

This poster discusses possible schemes for black-box MCSCF-like methods where the number of parameters describing the wavefunction scales algebraically with system size. A scheme is presented which is formulated as a coupled-cluster expansion with $O(N^2)$ amplitudes, and which automatically incorporates the most important static correlation effects.

Probing Excited States by Photoelectron Imaging: Dyson Orbitals within Equation-of-Motion Coupled-Cluster Formalism

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Angular distribution of photoelectrons (PAD) contains information about electronic wave functions and thus can be used to determine the nature of the state, as well as monitor its changes in the course of reactions. However, the interpretation of PADs in terms of molecular orbital composition of the ionized state is not straightforward. PADs are related to the so called Dyson orbitals, which can be as states of the leaving electron. Calculation of Dyson orbitals for the ground and excited states within equation-of-motion formalism is described and demonstrated by examples.

[P-14]

Fast and Exact: Predictions of Gibbs Free Energy of Intermolecular Complexes

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The theoretical study has been performed to refine the procedure for calculations of Gibbs free energy with a relative accuracy of less than 1 kcal mol⁻¹. Three benchmark intermolecular complexes are examined via several quantum-chemical methods, including the second-order Moller-Plesset perturbation (MP2), coupled cluster (CCSD(T)), and density functional (BLYP, B3LYP) theories augmented by Dunning's correlation-consistent basis sets. The effects of electron correlation, basis set size, and anharmonicity are systematically analyzed, and the results are compared with available experimental data.

The results of the calculations suggest that experimental accuracy can be reached only by extrapolation of MP2 and CCSD(T) total energies to the complete basis set. The contribution of anharmonicity to the zero point energy and $T\Delta S_{int}$ values is fairly small. The new, economic way to reach chemical accuracy in the calculations of the thermodynamic parameters of intermolecular interactions is proposed. In addition, interaction energy (D_0) and free energy change (ΔA) for considered species have been evaluated by Carr-Parrinello molecular dynamics (CPMD) simulations and static BLYP-plane wave calculations. The free energy change along the reaction paths were determined by the thermodynamic integration/“Blue Moon Ensemble” technique. Comparison between obtained values, and available experimental and conventional *ab initio* results has been made. We found that the accuracy of CPMD simulations is affected by several factors, including statistical uncertainty and convergence of constrained forces (TD integration), and the nature of DFT (density functional theory) functional. The results show that CPMD technique is capable of reproducing interaction and free energy with an accuracy of 1 kcal mol⁻¹ and 2-3 kcal mol⁻¹ respectively.

The Physical Origin of Chemical Phenomena

– Interpretation by Triadic Formula

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Throughout the past decades computational chemistry has become progressively important and has achieved full partnership with experiment as a research tool in all areas of chemistry. One of the major roles that theory has in modern chemistry is to provide quantitative elucidation and rationalization of molecular interactions and the energy associated with it. In this work we are presenting interpretation of three elementary, but extremely important reactions in chemistry and biochemistry – protonation, deprotonation and hydride ion addition reactions in the gas-phase based on triadic paradigm. Our approach is rooted in the separation of the interaction process into three distinct sequential steps. Considering protonation [1], it consists of: (1) ionization of an electron from the base in question to give radical cation, (2) attachment of the ejected electron to the incoming proton to form the hydrogen atom and (3) creation of the chemical bond between two newly formed radicals. Initial state effect of the base in question is mirrored through Koopmans' approximation $[\text{IE}(\text{B})_n]^{\text{Koop}}$, within which the energy required to eject a particular electron is equal to the negative of the HOMO or any other lower-lying orbital energy. The latter is the orbital corresponding to the lone-pair to be protonated as a rule. Relaxation energy of the produced radical (E_{relax}) gives intermediate stage in the protonation process, while homolytic bond association energy (BAE) reflects contribution arising from the final state effects of the protonated molecule. It follows that:

$$\text{PA}(\text{B}) = -\text{IE}(\text{B})_n^{\text{Koop}} + E_{\text{relax}} + \text{BAE} + 313.6 \text{ kcal mol}^{-1}; \quad \text{PA} = \Delta H \equiv \text{proton affinity} \quad (1)$$

By inspecting trends of changes in three terms appearing in triadic formula (1) one obtains an evidence of prevailing factor(s) influencing chemical reactivity. Utilizing this approach, we showed that, for example, basicity of methyl amines ($\text{NH}_{3-m}\text{Me}_m$; $m = 0-3$) increases, because it becomes easier to strip an electron from neutral molecule with every additional CH_3 group, leading to higher basicity – a clear initial state effect [1]. Such analysis was also applied to acidity of organic molecules, where the deprotonation reaction is considered as a reverse process – protonation of the conjugate base anion A^- . It turned out that the higher acidity of carboxylic acids over alcohols is dominated by the final state effects in most cases, or in other words by the properties of $\text{R}-\text{COO}^-$ anions [2]. An analogous scheme is easily designed to analyze and rationalize hydride affinities of molecules [3,4] or in treating substituent effects.⁵ In the former, the initial step is given by the attachment of an electron to the appropriate unoccupied molecular orbital of the molecule to be hydrided, following the ionization of H^- ion.

In summary, it can be safely concluded that the introduced methodology provides a versatile vehicle in elucidating interactions between any Lewis acid/base pairs being particularly effective in discussing trends of changes in chemical reactivity of closely related molecules.

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[P-16]

Search for Parity Violating Molecular Structures

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The existence of the weak force removes the otherwise exact degeneracy of enantiomers (chiral molecules that are mirror images of each other). It does so to an undetectably small degree for molecules that have been examined so far, justifying the belief common among chemists that the degeneracy is exact. However, it is conceivable that for a suitable choice of molecular structure this „parity violating effect” could be much larger and more easily observable. The quasirelativistic expression for parity violation energy has the form of a sum of scalar products of an axial and a polar vector, formally similar to the product encountered in the Rosenfeld formula for rotatory strength in natural optical activity. We have analyzed this expression and used the analysis for identifying conditions under which the parity violating term would be unusually large.

Analytic Gradients and Theoretical Spectroscopy with Perturbatively Corrected “Double Hybrid” Functionals

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In 2006 one of us (SG *J. Chem. Phys.* **2006**, *124*, 34108) suggested a new class of semi-empirical density functionals which incorporate – in addition to a fraction of the nonlocal Hartree-Fock exchange – also a fraction of nonlocal correlation. The latter was calculated at the level of second-order many body perturbation theory. The mixing ratios were found to be close to 50% HF exchange and 25% MP2 correlation. Owing to the incorporation of two sets of empirically determined nonlocal quantities, one may best refer to such functionals as of the “double hybrid” type. In conjunction with large basis sets, the new functionals showed a marked improvement in energetic benchmark calculations, e.g. an average error of 2.1 kcal/mol for mPW-2PLYP is the lowest ever obtained for a density functional (TS, SG *Phys. Chem. Chem. Phys.* **2006**, *38*, 4398). We have now considerably enhanced the applicability of the new functionals by deriving and implementing the relaxed densities and analytic gradients for these methods (FN, TS, SG, *J. Chem. Phys.* **2007**, in press). In this contribution, we will discuss results obtained for geometries, vibrational frequencies, polarizabilities, hyperfine couplings, spin-state energetics and also excitation energies. The results underline the large potential that the new functionals have for general chemistry applications including transition metal chemistry.

Accounting for Quasi-Degeneracy at the CCSD(T) Level*

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Single reference (SR) coupled-cluster (CC) methods account well for the dynamic correlation thanks to the exponential Ansatz for the wave operator, but are unable to properly describe the static and non-dynamic correlations arising, respectively, due to the degeneracy and quasi-degeneracy of references. Consequently, these methods may fail when describing the breaking of genuine chemical bonds, biradical species, reaction intermediates or open-shell systems in general.

We approached this problem via a multireference (MR) CC formalism of either a genuine state-universal (SU) or a state-speci_c (SS) type. In the MR SU case we developed a general-model-space (GMS) SU MR CCSD formalism by introducing the so-called *C-conditions* for the internal cluster amplitudes.¹ In either case we have also employed the so-called *externally-corrected* (ec) CC approach, which uses a small subset of the most important higher-than-pair cluster amplitudes that are extracted from a suitable external source. As the best source proved to be modest-size MR CISD wave functions thanks to the complementarity of the CI and CC approaches in their handling of the dynamic and non-dynamic correlations. This resulted the $(N;M)$ -CCSD ($M \leq N$) method² (employing M wave functions of the N -reference CISD as an external source for an M -reference SU CCSD) in the MR case and in the reduced MR (RMR) CCSD method³ in the SR case.

The above mentioned GMS SU and RMR CCSD methods correct for the most important triples and quadruples (Ts and Qs) from the first order interacting space, which we can refer to as the *primary* Ts and Qs. These are responsible mainly for the non-dynamic correlation and represent only a small subset of all Ts and Qs that consists of both the primary and the *secondary* Ts and Qs. Neglecting the latter and correcting for the secondary Ts via the standard additive (T)-type correction, we arrive at the GMS CCSD(T) and RMR CCSD(T) methods.⁴

Here we shall focuss on some applications of the RMR CCSD(T) method⁴ to systems for which SR CCSD(T) fails even at the equilibrium geometry,⁵ as well as for barrier heights of 19 chemical reactions⁶ and transition metal ion – methylene complexes.⁷

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A London-Type Formula for the Dispersion Interaction in Endohedral A@B Systems

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In 1930 London derived his famous R^{-6} expression for the leading term of the dispersion interaction between two closed-shell systems. We have derived the analogous expression for the case when one subsystem A is inside the other subsystem B. The expression has no explicit dependence on R and involves both the usual static dipole polarizability α^1 at A and a new type of polarizability, α^2 at B. The latter is calculated directly and the obtained interaction energies are compared with MP2 calculations on a M@C₆₀ supermolecule with M = He-Xe; Zn-Hg; CH₄.

QM/QM Electronic Embedding for Electronic Structure Studies of Surface Chemistry

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An accurate first-principles treatment chemical reactions on surfaces continues to be a significant challenge facing the computational chemistry community. As the principal limitation is tied to system size, investigations of reactive surface chemistry frequently employ embedded cluster models where the number of heavy atoms can be minimized. Hybrid models, such as QM/MM and QM/QM schemes, are a promising avenue for modeling large surface segments. Because of our focus on surface chemistry involving systems where MM or semiempirical parameters may not be available, a QM/QM scheme is of particular interest. However, in almost all QM/QM applications published in the literature thus far, only a mechanical embedding scheme is used and coupling between the two regions is treated only mechanically with the wavefunction in the central region unaffected by the electrons of the environment. We are presently developing a sequence of electronic embedding schemes for more realistic simulations. The resulting hierarchy, where the treatment ranges from simple point charge embedding to interaction integrals in the Hamiltonian matrix, will be discussed. We will also describe our current development status and present results from initial applications to ongoing studies of silicon and silicon oxide surface chemistries.

Quadratic Description of Conical Intersections: Characterization of Critical Points on the Extended Seam: 1,3-Butadiene Case Study

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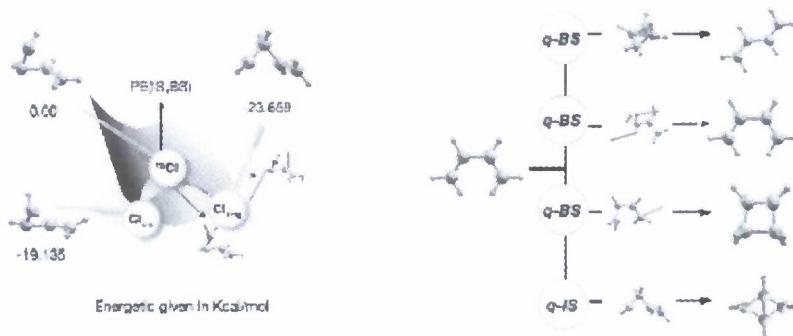
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Conical intersections are more often invoked in the rationalization of chemical processes where the pathway involves more than a single potential energy surface, *i.e.* non-adiabatic processes. Recently, we have developed a second-order description of the crossing seam and the potential energy surfaces around it. This analysis enables one to compute frequencies and normal modes of a molecule at a conical intersection geometry within the intersection space. Accordingly one can establish whether the conical intersection geometry optimized is either a saddle point or a minimum on the crossing hyper-line. In the first case, the seam transition vector can be exploited to locate other conical intersection points at lower energy. The connection amongst the optimized conical intersection points is then computed with a constrained conical intersection optimization and confirmed by intersection-space intrinsic reaction coordinate calculations. Characterization of the CI seam in Butadiene will be given as an example



The potentialities of this quadratic analysis are illustrated by analysing the S₀/S₁ seam of 1,3-butadiene. It will be shown how topological considerations about the crossing PESs may be used to predict successfully the photoproducts of 1,3-butadiene.



**An Accurate ab Initio Potential Energy Curve of F₂,
Yielding an Accurate Vibration-Rotation Spectrum,
Through CEEIS Evaluation of Electron Correlation**

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The recently introduced method of *correlation energy extrapolation by intrinsic scaling (CEEIS)* is used to calculate the non-relativistic electron correlations in the valence shell of the F₂ molecule at 13 internuclear distances along the ground state potential energy curve. Using Dunning's correlation-consistent double-, triple- and quadruple-zeta basis sets, the full configuration interaction energies are determined, with an accuracy of about 0.2–0.3 mE_h, by successively generating up to eight-tuple excitations with respect to multiconfigurational reference functions that strongly change along the reaction path. The energies are then extrapolated to their complete basis set limits. These nonrelativistic, valence-shell-only-correlated energies are complemented by the energy contributions that arise from electron correlations involving core electrons, from spin-orbit coupling and from scalar relativistic effects. The dissociation curve is found to rise rather steeply towards the energy of the dissociated atoms because, at larger distances, the atomic quadrupole repulsion as well as the spin-orbit coupling both counteract the attractive contributions from incipient covalent binding and correlation forces including dispersion. An analytical expression for the potential energy curve is found in terms of eventempered Gaussian exponentials by fitting the *ab initio* energies with a mean absolute deviation of about 0.05 mE_h. With this analytical potential energy curve, the full vibrational and rotational energy spectrum of F₂ is calculated using the discrete-variable-representation. The mean absolute deviation of the theoretical levels from the experimental levels, which had been measured in the Herzberg Institute by high-resolution electronic spectroscopy, is about 5 cm⁻¹ over all 22 levels. The Dunham analysis of the spectrum is found to be very accurate. The dissociation energy with respect to the lowest vibrational energy is calculated to be 12 931 cm⁻¹, differing from the experimental value of 12 920 \pm 50 cm⁻¹ within experimental uncertainty. The agreement of the theoretical spectrum and dissociation energy with the experimental values is contingent upon the inclusion of the effects of core-generated electron correlation and spin orbit coupling. The results establish the effectiveness of the CEEIS method along a reaction path where strongly multi-configurational reference functions change strongly.

Full Accuracy Local MP2Svein Saebo*Mississippi State University, Mississippi State, MS 39762, U.S.A.*Peter Pulay*Department of Chemistry and Biochemistry, University of Arkansas
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Recently, we have proposed a low-scaling method for full-accuracy second order Moller-Plesset (MP2) calculations. This method uses only natural sparsity, and thus yields results which are essentially numerically identical with the traditional canonical results. In contrast to other LMP2 schemes, this method avoids introducing a new model chemistry, and it is free from localization artifacts.

Pair correlation can be classified as *strong* or *weak*. Physically, these two types are quite different. Strong pair correlation, which includes intrapair correlation, and correlation between neighboring localized orbitals that overlap significantly, is dominated by short-range interaction. Weak pair correlation is dispersion attraction between non-overlapping charge densities, and its magnitude is much smaller.

In our first implementation, we used a fixed domain for a given occupied orbital, regardless of its pair partner, i.e. whether it was participating in a strong or weak correlation. As a result, most of the computational effort was spent in the LMP2 iterations involving weak pairs, in spite of their modest contribution to the correlation energy.

A simple solution to accelerate these calculations would be to use reduced domains for the weak pairs. It is obvious that the large local basis sets used in our current program are not required for weak pairs. A more efficient solution is, however, to exploit the physical nature of weak correlation as dispersion energy between distant, nonoverlapping orbitals to reduce the size of the virtual space.

We will describe the set of molecular orbitals, called dispersion orbitals, used to describe weak pairs, and we will demonstrate that a relatively small number of well-chosen MOs are sufficient to accurately describe weak pairs. Test calculations demonstrating accuracy and scaling of the method will be presented.

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Heuristic Chemistry

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Computational methods are typically employed to rationalize experimental findings such as molecular structures and spectroscopic data *after the fact*. It is clear, however, that the true strength of computational chemistry is the *prediction* of new, hitherto unknown structures and reactions. In an ideal situation, this would greatly reduce experimental effort and, consequently, time and resource allocations. The key problem is that although many computational methods have been well-tested on a limited set of structures, weaknesses of particular methods sometimes unexpectedly surface; examples will be presented that emphasize this to be particularly true for DFT methods [1]. Helpful along this way are reactions or structures which are similar enough to allow a relatively save interpretation and *extrapolation*, i.e., “families of reactions.” A highly practical approach is to search systematically for new reactions and to group them into “structural families” so that they can be rationally understood and new reactions can be identified [2]. For instance, the 6-electron-family of reactions can be grouped into 6π (e.g., Cope, allenyl-Cope) and $[2s+4\pi]$ systems (e.g., Bergman, Myers-Saito). With this rationalization at hand, we were *inter alia* able to derive rules for when to expect biradicals along such reaction paths; this question kept much of the “Cope” community occupied for many years. We find that biradical intermediates are involved if they are stabilized by allylic resonance or aromaticity. We firmly believe that such *heuristic* approaches utilizing theory are highly useful not only for understanding and grouping reactions but also for teaching purposes [3].

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The Rare Gas Packing Problem

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Kepler's conjecture (1611) states that fcc (or hcp) has the tightest possible packing, so that no other arrangement of higher density could be found, Fig.1. Only very recently a proof of this famous theorem has been provided by T. C. Hales. At the quantum level this hard-sphere model is not applicable anymore. For example, all realistic two-body interaction potentials (like a Lennard-Jones potential) show a energetic preference of the hcp over the fcc structure. However, all rare gases crystallize in fcc. This two-body dilemma was first identified by Max Born in 1940 and was unresolved up to now. Maddox stated in 1988 that "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition." And Young stated in 1991 that "There has not been a satisfactory explanation of why rare gas solids exist in a face-centered-cubic (fcc) phase rather than a hexagonal-close-packed (hcp) phase." We demonstrate that the Lennard-Jones potential will always prefer the hcp structure. We extend the two-body Lennard-Jones potential to obtain analytical expressions for the lattice parameters, cohesive energy and the bulk modulus using the parameters of Lennard-Jones and Ingham, which we evaluate up to computer precision for the cubic lattices and hcp. The inclusion of three-body terms does not change the preference of hcp over fcc, and zero-point vibrational effects are finally responsible for the transition from hcp to fcc. More precisely, it is the coupling between the harmonic modes which leads to the preference of fcc over hcp, as the simple Einstein approximation of moving an atom in the static field of all other atoms fails to describe this difference accurately. Hence this long-standing problem can now be considered as solved. Lattice dynamic calculations produced specific heats for Ne, Ar and Kr in good agreement with experiment.

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Electronic Wave Function Expansions Using a Novel Nonlinear Basis

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A new expansion basis [1-4] for electronic wave functions has been introduced. In this approach, the wave function is written as a linear combination of *product basis functions*, and each product basis function in turn is formally equivalent to a linear combination of configuration state functions (CSFs) that comprise an underlying linear expansion space of dimension N_{csf} . The CSF coefficients that define the basis functions are nonlinear functions of a smaller number of variables $N_{\phi} \ll N_{\text{csf}}$. The method is formulated in terms of spin-eigenfunctions using the Graphical Unitary Group Approach (GUGA), and consequently it does not suffer from spin contamination or spin instability. The expansion form is appropriate for both ground and excited states and to closed- and open-shell molecules.

Efficient procedures to compute hamiltonian matrix elements and reduced one- and twoparticle density matrices for this nonlinear expansion have been developed. The effort required to construct an individual hamiltonian matrix element between two product basis functions $H_{MN} = \langle M | \hat{H} | N \rangle$ scales as $O(\beta n^4)$ for a wave function expanded in n molecular orbitals. The prefactor β itself scales between N^0 and N^2 , for N electrons, depending on the complexity of the underlying Shavitt Graph. The corresponding metric matrix element $S_{MN} = \langle M | N \rangle$ requires effort that scales as $O(\beta n)$, the one-particle transition density \mathbf{D}^{MN} requires $O(\beta n^2)$ effort, the two-particle density \mathbf{d}^{MN} requires $O(\beta n^4)$ effort, and the gradient of the energy with respect to the nonlinear parameters requires $O(\beta n^5)$ effort. There is no component of the effort or storage for matrix element computation or wave function optimization that scales as N_{csf} . Timings with our initial implementation of this method are very promising; e.g. a hamiltonian matrix element involving product basis functions corresponding to an underlying linear expansion space dimension $N_{\text{csf}} \approx 10^{25}$ requires only 10 to 15 seconds on a laptop or desktop computer. An energy-based optimization approach has been developed and applied to the nonlinear wave function parameters; this exploits *partially contracted functions* in order to reduce the dimensionality of the optimization problem at each step and to minimize the number of expensive gradients that must be computed.

Some initial results directed toward qualitative wave function interpretation based on the concepts of *node density* and *arc density* will be presented; this analysis is necessary with such large wave function expansions. Convergence, of both the valence correlation energy and dynamical correlation energy, with respect to the product basis expansion length N_a will be discussed. Some new closed-form expressions for various Shavitt Graph and Auxiliary Pair Graph statistics will be presented.

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Theoretical Studies of Mechanisms for Low-energy Electron Damage to DNA

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Stimulated by the observations of Boudaiffa et al.¹ that low-energy (3.5-20 eV) electrons can induce strand breaks in DNA (probably via core-excited resonance states) and knowing of the work of Burrow et al.² on π^* shape resonances in DNA bases, we explored the possibility that shape resonances could cause damage to DNA. In a series of publications [3-8], we employed stabilization-type electronic structure methods and potential energy landscape exploration techniques to address this question. The systems we examined included small fragments of DNA each of which included at least one base, one sugar, and two phosphate units. We also studied sugar-phosphate-sugar units as part of an investigation of electron attachment to phosphate P=O π^* orbitals. Our efforts allowed us to predict that electron attachment to form a low-lying (0.2-2 eV) π^* shape resonance of a base unit could cause a sugar-phosphate C–O bond to be rendered susceptible to fragmentation over barriers ranging from 5 to 25 kcal mol⁻¹, but only when the phosphate group has a counter-cation nearby. The rates of C–O bond rupture were predicted to be as high as 10¹⁰ s⁻¹ which, considering the ca. 10¹⁴ s⁻¹ detachment rates of the π^* resonance, suggest a yield of one strand break in 10⁴ attached electrons. We also considered base-sugar N–C and base N–H bond cleavage induced by attachment to a base π^* orbital, but found their barriers to fragmentation significantly higher than for sugar-phosphate C–O cleavage. We explained the preference for C–O bond rupture in terms of the very high electron affinity of the phosphate radical formed when this bond is broken. In addition, we considered the possibility of attaching a low-energy electron to a phosphate P=O π^* orbital, but suggested that this would occur only for electrons having kinetic energies in excess of 2 eV. Subsequent to our predictions that shape resonances can cause strand breaks and that C–O bond rupture should dominate, new experiments [9] involving both the Sanche and Burrow groups showed that single strand breaks, whose yield-vs-energy profiles tracked the base π^* electron attachment cross-sections, could indeed be caused by electrons below 3.5 eV and even below 1 eV. In addition, very recent experiments[10] from the Sanche group on DNA oligomers showed, by chemical analysis of the products of strand break formation, that indeed sugar-phosphate C–O bond cleavage is the dominant outcome of single strand break formation caused by low-energy electrons.

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How to Obtain the Correlation Energy from the Hartree-Fock Density Matrix?

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Several methods of linear-scaling Hartree-Fock calculations [1-3] yield the density matrix P directly, avoiding the diagonalization of the Fockian. At the end of these calculations, one knows P but one does not know the molecular orbitals MOs. To obtain the correlation energy in such a situation, one may follow two alternative routes: (i) one tries to write [4] the correlation energy as an explicit functional of P , or (ii) one constructs localized molecular orbitals from P , and applies any of the local correlation schemes. We advocate the use of frozen localized molecular orbitals (FLMOs). In this approach localized orbitals are constructed in an iteration-free manner by projection with P only for a selected 'active part' of a large molecular system. These active LMOs enter the correlation calculations, while the others, which are never explicitly constructed but are hidden in P , are considered tacitly frozen.

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Accurate MP2 Correlation Energies from Mixed Gaussian-Type Orbital and Gaussian-Type Geminal Basis Sets

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We have implemented the use of mixed basis sets of Gaussian one- and two-electron (geminal) functions for the calculation of second-order Moller–Plesset (MP2) correlation energies. We shall describe some aspects of the formalism and our implementation, with particular emphasis on the different forms chosen for the pair functions, and present We have implemented the use of mixed basis sets of Gaussian one- and two-electron (geminal) computational results for some closed-shell systems. Our calculations indicate that the method presented is capable of yielding highly accurate second-order correlation energies with rather modest Gaussian orbital basis sets, thus providing an alternative route to highly accurate wave functions. For the neon atom, the hydrogen molecule, and the hydrogen uoride molecule, our calculations yield the most accurate upper-bound MP2 energies available.

The Reductive Half-Cycle of Aldehyde Oxidoreductase: A QM/MM study

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Hydroxylation reactions of aromatic and carbonylic carbon atoms are typical for molybdopterin (MOP) containing enzymes belonging to the Xanthine Oxidase family. In these reactions, water instead of O_2 is used as a source of oxygen, with the oxygen being transferred to the substrate after the hydroxylation reaction has occurred [1]. The reductive half of the enzymatic cycle, i.e. the interconversion of acetaldehyde to acetic acid, is performed by Aldehyde Oxidoreductase (AOR). At the first stage of the enzymatic cycle, the MOP cofactor is reduced from Mo(VI) to Mo(IV), see Figure 1. To regenerate the Mo(VI) species, electrons are transferred through a chain of two $[Fe_2S_2]$ clusters and are subsequently used to oxidize O_2 or NAD^+ .

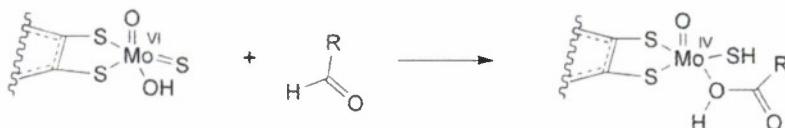


Figure 1. The reductive half-cycle of Aldehyde Oxidoreductase.

To investigate the reductive half-cycle of Aldehyde Oxidoreductase, accurate QM/MM models of AOR are investigated. The models were generated starting from a crystal structure of AOR [2] which contains the isopropanol inhibitor. The inhibitor was substituted for the acetaldehyde substrate and a spherical solvation model was applied. For consistency with the previous gas-phase calculations of Zhang et al. [3,4] the B3LYP functional is used throughout this study. For the interconversion of acetaldehyde to acetic acid, three different pathways have been investigated:

- A one-step mechanism, where the C-O bond formation and the hydride transfer from the aldehyde to the equatorial sulfur atom proceed at the same time.
- A metal center activated pathway, where the carbonylic oxygen approaches the molybdenum center during the C-O bond formation. After reorientation of the formed semi-acetal intermediate, a formal hydride transfer is observed, accompanied by reduction of the molybdenum center from (VI) to (IV).
- A three-step mechanism, starting with a deprotonation of the hydroxy ligand on the molybdenum cofactor by the nearby GLU869 side-chain, which then forms a hydrogen-bonded complex with the substrate. This is followed by C-O bond formation and a final hydride transfer, as already found for the metal center activated pathway.

Based on energetic considerations, the reductive half-cycle appears to follow the three-step reaction mechanism.

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The Reaction Force: Concept and Applications

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The concept of the reaction force is presented and discussed in detail [1-3]. For typical processes with energy barriers, it has a universal form which defines key points along an intrinsic reaction coordinate: the force minimum and maximum. The three resulting regions along the reaction coordinate can be interpreted as involving preparation of reactants in the first, transition to products in the second, and relaxation in the third. This general picture is supported by the distinctive patterns of the variations in relevant global and local electronic properties such as chemical potential, hardness, electronic flux, charges and Fukui functions. An important feature of the reaction force analysis is that the activation barrier is shown to be composed of two terms, representing the initial preparatory stage and the first part of the transition stage. We identify this second term as an “effective electronic activation energy.” Taking account of these two contributions to the activation energy can help significantly in understanding reaction mechanisms. Few applications to the analysis of different kind of chemical reactions are presented.

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**Recasting the 2-Body:*n*-Body Treatment for Weakly Bound Clusters
in the ONIOM Formalism: Efficient and Accurate QM:QM
Methods for Hydrogen Bonding and π Interactions**

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A highly efficient integrated (or hybrid) QM:QM technique for the description of weakly bound clusters is presented. By taking advantage of the recently developed multicentered integrated QM:QM methods [J. Comput. Chem., 24, 1563-1568 (2003); Mol. Phys., 103, 309-315 (2005)], it is possible to recast the classic 2-body:*n*-body treatment of weakly interacting clusters in the ONIOM formalism. This formulation allows the technique to (1) be extended to analytical 1st and 2nd energy derivatives and (2) readily take advantage of the latest developments in high-accuracy electronic structure theory for weak interactions. This integrated approach is extremely efficient since it essentially reduces the problem to a series of dimer calculations with the high-level method and one low-level calculation on the entire cluster. It is also extremely accurate. When properly applied to small weakly interacting clusters (e.g., diacetylene trimer, cyanogen trimer, $(HF)_n$, $(H_2O)_n$, He_n , Ne_n , $n = 3-5$), the multicentered QM:QM methods are typically 1-3 orders of magnitude faster than the high-level method while introducing an error of less than 1% in the interaction energy.

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**Hartree–Fock stability and broken symmetry solutions
of O²⁻ and S²⁻ anions in external confinement. HF and CCSD(T)
polarizabilities of confined O²⁻, S²⁻, and F⁻ anions***

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We study the effect of a confining potential [1] on systems that exhibit Hartree–Fock (HF) instabilities [2], and thus admit broken symmetry (BS) HF solutions, using the O²⁻ and S²⁻ doubly-charged anions as model systems [3]. With the increasing strength of the external harmonic confinement potential, $W(r) = 1/2(\omega r)^2$ the BS solutions are systematically eliminated. We use extended doubly-augmented Gaussian basis sets up to and including d-aug-cc-pV6Z and find that the number and the character of BS solutions exhibit significant basis set effects. These basis sets were further extended by additional ghost basis functions, located away from the atomic centre. The role of the electron correlation effects for the BS HF solutions was examined by the CCSD(T) method. In addition to modelling the confinement by the harmonic-like potential $W(r)$, we also examined a more realistic “confinement”, realized by a grid of point charges modelling the crystal structure of MgO. Again, we find that the HF instabilities and the implied BS solutions disappear with the increasing magnitude of the model charges simulating the crystal environment. At the same time, the O²⁻ anion is energetically stabilized with respect to both the O- anion and the neutral oxygen atom [3]. We also report [4] considerable changes of dipole polarizabilities of O²⁻, when embedded in the confining $W(r)$ potential or in the grid of point charges modelling the crystal structure of MgO [5]. Analogous calculations are presented for the S²⁻ and F⁻ anions. The analysis of the BS solutions allows us to control the physical relevance of calculated molecular properties of systems which potentially exhibit HF instabilities.

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A Water-mediated and Substrate-Assisted Catalytic Mechanism For Adenosine Deaminase

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Adenosine deaminase (ADA) is an essential enzyme in purine metabolism, catalyzing the deamination of adenosine or deoxyadenosine to their respective inosine product. ADA deficiency is associated with severe combined immunodeficiency disease (SCID), which makes ADA a paradigm for structure-function studies of a genetic disease¹. Although with extensive studies on the catalytic mechanism of ADA, several critical steps remain to be elucidated². The full reaction pathway catalyzed by ADA is explored using two-layer ONIOM method. The results suggested a novel water-mediated and substrate-assisted mechanism: Glu217 acts as the general base to activate the zinc-coordinated water, this proton transfer process is mediated by a bridging crystal water molecule, and further stabilized by the substrate binding. The protonated Glu217 then acts as general acid to activate the substrate by the protonation of N-1. The protonation of the leaving amino group mediated by His238 is the rate-determining step in the reaction pathway, which is unexpected in the previous proposed mechanism, but more consistent with the experimental studies³. Our results also shed light on the catalytic mechanism of other members of amidohydrolase superfamily.

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Unusual Substituent Effects on the Bonding of Iminoboranes

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Substituent effects on iminoboranes XBNH, HBNX and XBNX (X = H, CH₃, NH₂, OH, F) have been analyzed in the framework of the NBO, AIM and ELF approaches, using B3LYP/6-311++G(d,p) optimized geometries and electron densities. Boron-substituted derivatives, XBNH, are more stable than the corresponding nitrogen-substituted isomers HBNX, with the energy difference increasing as the electron withdrawing character of the substituent increases. The BN linkage is not much affected by N-substitution, but it is significantly altered when the substituent is attached to the boron atom in both XBNH and XBNX series of compounds. Moreover, substituent effects on the structures of iminoboranes are opposite those observed for the corresponding isoelectronic acetylene derivatives. The ELF analysis indicates that electron-withdrawing substituents enhance the localization of electrons in a torus around the CC or the BN axis. As a result, although electron density is depleted at the bcp the bond does not necessarily become weaker, since density increases around the periphery, a phenomenon named the “hole” effect. The dissimilarities between acetylene and iminoborane derivatives are primarily a consequence of the significant distortion of this torus in the latter, due to the large difference between the electronegativities of B and N, which leads to a large contribution of the X-B=N-Y resonance structure in some cases. The “hole” effect is reflected in a reasonable correlation between the Laplacian of the electron density at the bcp and the BN bond length.

FIRST POSTER SESSION

[Pl-1]

Nucleobase-Fluorobenzene Interactions: Hydrogen Bonds or π - π Stacking?

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We have performed accurate electronic-structure calculations on the hydrogenbonded and π -stacked complexes of 2-pyridone with three different n-fluorobenzenes (1,2,4,5-tetrafluorobenzene, pentafluorobenzene and hexafluorobenzene). The binding energies of these complexes were calculated by adding the contributions from four levels of theory, using the largest possible basis at each level

$$\Delta E = \Delta E_{HF}^{aVQZ} + \Delta E_{RIMP2R12}^{aVQZ} + \Delta E_{CCSD}^{aVDZ} + \Delta E_{CCSD(T)}^{aVDZ'}$$

Our results show that the complexes of 2-pyridone with tetrafluorobenzene and pentafluorobenzene are more stable than their π -stacked analogues. This picture is in very good agreement with the recent experimental work carried out by the group of Leutwyler in Berne, Switzerland.^{1,2} The fluorescence emission spectra show that the nucleobase analogue 2-pyridone forms exclusively hydrogen bonded complexes with tetrafluorobenzene and pentafluorobenzene. In contrast, the 2-pyridone hexafluoro-benzene complex is only experimentally observed in the π -stacked form. The good agreement with the experiment was obtained due to the inclusion of correlation effects at the CCSD and CCSD(T) levels.

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[Pl-2]

Computational Study of the Substitution Effect on N-B Bond in Ammonia-Borane Complexes

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The Lewis acid-base $H_{3-n}F_nN-\tilde{B}F_mH_{3-m}$ ($n = 0 \sim 3$; $m = 0 \sim 3$) system was examined using the density functional theory calculations. The N-B bond strength can be adjusted stepwise by increasing the number of substituted fluorine atoms. The main finding of this work is the bond distances of the complexes do not correlate directly with the bond strengths. Some rationalization of this interesting observation was provided by HOMO-LUMO interaction and electrostatic interaction.

[PI-3]

Umbrella Integration: A Novel Analysis Method for Umbrella Sampling Simulations

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We present a method to analyze biased molecular dynamics (MD) and Monte Carlo (MC) simulations, also known as umbrella sampling. In the limiting case of a strong bias, this method is equivalent to thermodynamic integration. It employs only quantities with easily controllable equilibration and greatly reduces the statistical errors compared to the standard weighted histogram analysis method (WHAM). The statistical error associated with the resulting free-energy differences can be estimated. We show the success of our approach for two examples, one analytic function, and one biological system.

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[PI-4]

A Study of Energies and Electronic Properties of Water Clusters Using the Hirshfeld Method

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The structure and properties of small water clusters has been the subject of intense experimental and theoretical research in the last decade, seeking understanding of the interactions between water molecules themselves and between water and a solute. The structure of water clusters, because of the hydrogen bonds present, forms a link between single water molecules and bulk water. Because of their low symmetry, the study of clusters of increasing size reveals properties of the hydrogen bonds the molecules make, which are otherwise hidden in homogeneous condensed phases. Hydrogen bonding is a kind of dipole-dipole electrostatic interaction, making electronic properties of the molecules in the clusters, such as dipole moment and polarizability, essential for characterizing these interactions. This study considers the effect of structural parameters on the local dipole moments and polarizabilities of a molecule in a cluster, properties that may open new roads to understanding many-body water interactions and allow building improved and transferable local force fields. Additionally, the energies of the water molecules in the clusters are analyzed and the eventual presence of a cooperative effect for the formation of hydrogen bonds is investigated. The dipole moments, polarizabilities and energies are partitioned by methods based on the Hirshfeld scheme. The values of those properties of the water molecules within the clusters depend on the hydrogen bonds a molecule makes with its neighbors. A molecule having more hydrogen bonds is found to have a smaller dipole moment, a smaller polarizability and a higher energy. The relation with the strength of the hydrogen bond and the different molecular contributions is analyzed.

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[Pl-5]

Ab Initio Studies of the Complexes Formed Between Molecular Oxygen and Carbon Dioxide, Carbonyl Sulphide, and Carbonyl Disulfide

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The van der Waals complexes formed between singlet and triplet molecular oxygen as electron donors, and carbon dioxide, carbonyl sulphide and carbon disulphide as electron acceptors, have been studied by means of *ab initio* molecular orbital theory. The calculations were carried out using the Gaussian98 program, at the level of second order Moller-Plesset perturbation theory, with a triple-zeta Gaussian basis set with polarization and diffuse functions on all atoms. The structures were optimized and the interaction energies were computed and corrected for basis set superposition error and zero-point vibrational energy differences. The interaction energies were correlated with a number of physical properties of the electron acceptors. The vibrational spectra were calculated, and the harmonic wavenumbers of the complexes were compared with those of the unperturbed monomers, in order to determine the effect of complexation on the spectra of the monomer species. The wavenumber shifts so obtained were then correlated with the computed interaction energies. These studies complement a similar series of calculations of the analogous complexes of molecular nitrogen [1], carbon monoxide [2] and ozone [3] as electron donors and the properties of all four families have been compared.

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[Pl-6]

Analytic gradient method in nuclear orbital plus molecular orbital (NOMO) theory: Evaluation of averaged bond distance

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This paper extends the formulation of the analytic gradient method by Pulay [1] to the NOMO theory [2], which simultaneously determines nuclear and electronic wave functions without the Born-Oppenheimer approximation. The formulations correspond to the translation- and rotation-contaminated (TRC), translation-free (TF), and translation- and rotation-free (TRF) treatments [3]. The optimizations of the orbital centers for several diatomic molecules give the averaged nuclear distances $\{R_0\}$ reflecting the quantum effects of nuclei and the anharmonicity of the potential energy surfaces. The numerical assessments have clarified that the effects of eliminating the translational and rotational contaminations, *i.e.*, the TRF effects are important to improve the evaluations of $\{R_0\}$, especially for the molecules including hydrogen atoms.

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[Pl-7]

Anharmonic vibrational calculations on noble-gas-containing methyl halides

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In recent years a renaissance in noble gas chemistry has taken place. The chemistry of carbon-xenon compounds is one of the newest aspects of organoelement chemistry. The number of known Xe-C compounds is still limited but these molecules are considered as potentially efficient precursors in synthetic organic chemistry. Here, quantum chemical calculations have been performed on novel compounds that may expand the scope of noble gas chemistry. These molecules are insertion compounds of various noble gas atoms into methyl halides. The xenon-compounds form the most stable group of these molecules but a few species containing krypton and argon are predicted to be stable as well. In order to facilitate the experimental detection of such species, also their infrared spectra have been computed. The harmonic vibrational calculations are supplemented with anharmonic vibrational calculations based on the cc-VSCF method. This allows us to predict the overtones and combination transitions in addition to the fundamental ones.

[Pl-8]

Linear-Scaling MP2 Methodologies Based on the Divide-and-Conquer Method: Novel Local Treatment of Electron Correlation

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In this presentation, we propose two linear-scaling schemes for obtaining the approximate second-order Moller-Plesset perturbation (MP2) energies within the framework of the divide-and-conquer (DC) method of Yang [1]. One is based on the density matrix (DM) obtained from the DC Hartree-Fock (HF) calculation [2]. In this method, which we call DC-DM MP2 [3], the DC-HF DM is applied to the explicit MP2 correlation energy functional [4-6] standing on the AO-Laplace MP2 [4]. The other is based on the local treatment of the electron correlation. This method, which we call DC-MP2 [7], evaluates the correlation energy of the total system by summing up subsystem contributions. The correlation energy corresponding to a subsystem is calculated from subsystem orbitals based on a scheme for partitioning the correlation energy, which is derived by analogy with the energy density analysis (EDA) [8]. Numerical assessments revealed that these schemes provide reliable correlation energies with less computational costs than the conventional MP2 calculation in large-system calculations. Particularly, the DC-MP2 gives near-linear time performance with respect to the system size.

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[PI-9]

On the Dependency of Correlation Energy and Zero-Point Energy on the Nuclear Frame and Number of Electrons in Molecular Systems

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Recently we have developed twin methods, REBECEP (Rapid Estimation of Basis Set Error and Correlation Energy from Partial Charges) [1-3] for correlation and basis set error calculation and REZEP (Rapid Estimation of Zero Point Energy from Partial Charges) [4-6] for zero point energy estimation, both from atomic partial charges. We used databases of G2 and G3/99 total energies, as well as scaled HF-SCF/6-31G(d) zero point energies, both with certain atomic partial charges of more than one hundred closed shell neutral molecules containing H, C, N, O, and F atoms. Our method showed near 1.0 kcal/mol average absolute deviation from the experimental results with much less computational time and disc space demand. In this respect, we carry out some statistical analysis to establish a plausible physical background for the parameters of these two empirical methods. The dependency, indicated in the title, is very interesting in the general theory of correlation energy [7-8] and zero point energy as well.

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[PI-10]

Iterative Subspace Optimization, Extensions to Geometry DIIS

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The original GDIIIS method [1] proved to be a very efficient and simple tool for optimizing small molecules. Since GDIIIS tends to converge to the closest critical point of the potential energy surface it should be controlled [2] or modified [3] to ensure convergence to a desired type of critical points. The present work proposes a new formalism, called iterative subspace optimization, via utilizing a non-symmetrical Hessian-like matrix in conjunction with rational function optimization (RFO)[4]. For the purpose of optimizations in a molecular mechanics environment ensuring a conjugate step is possible.

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[PI-11]

Proton Magnetic Shielding Tensors of Aromatic Compounds. From the Individual Molecule to the Crystal

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It may be surprising that in 2006, almost 200 years after the discovery of benzene [1], the proton shielding tensor in solid phase benzene was still unknown. The computation of this quantity is interesting for three reasons. First, benzene is the prototype aromatic system. Second, the experimental determination of the benzene proton shielding tensors, which requires a single-crystal sample and a measurement temperature below 40 K [2], is presently nearly impossible. Third, the individual molecule proton shielding tensors are, effectively, not measurable quantities, because in both single-crystal and powder samples these properties are strongly affected by the surrounding molecules [3]. If computed proton shielding tensors are to be compared with experimental results, computations must include the crystal environment. This study reports the computation of both the local and intermolecular (crystal) contributions to the proton shielding tensor of benzene [4] using a method benchmarked on the solid-state crystal of biphenyl [2]. It is shown that a spherically shaped crystal environment must be extended to a radius of at least 20 Å to properly account for the intermolecular shielding contributions. The isotropic shieldings of the three distinct protons [5,6] are modified by as much as 1.7 ppm by the crystal environment. The anisotropy of the shielding tensor is increased by up to 4.51 ppm.

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[PI-12]

Analytic Gradients for Hilbert-Space Multireference Coupled-Cluster Methods

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We present analytic gradient theory and its pilot implementation for several versions of multireference Hilbert-space coupled-cluster methods. The analytic gradient has been derived for (i) Brillouin–Wigner (BWCC) method, (ii) BWCC method with the iterative size-extensivity correction, (iii) state-universal Hilbert-space MRCC method, and (iv) Mukherjee’s state-specific MRCC method. The presented pilot implementation is based on full-Cl expansions and the analytic gradients have been verified with respect to numerically computed ones on the example of methylene molecule. For Brillouin–Wigner MRCC method, the resulting lambda- and gradient- equations do not contain terms explicitly mixing amplitudes of different reference configurations and can thus be implemented in an efficient way.

[PI-13]

Modeling of High-Order Many-Body Terms in the Expansion of Multidimensional Potential Energy Surfaces - Application to Vibrational Spectra

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The calculation of accurate vibrational spectra requires the calculation of large fractions of the multidimensional potential energy surface around the equilibrium structure. Using a many-mode expansion given by

$$V(q_1, q_2, \dots, q_n) = \sum_i V_i(q_i) + \sum_{i < j} V_{ij}(q_i, q_j) + \sum_{i < j < k} V_{ijk}(q_i, q_j, q_k) + \dots,$$

it is sufficient for most applications to truncate this series after the 3D terms (V_{ijk}). Consequently, the calculation of these terms is the computational bottleneck within the generation of the potential. Here we present first benchmark calculations in which the 3D terms were modeled by reparametrized semiempirical methods in a fully automated fashion, while 1D and 2D terms were generated by high level *ab initio* calculations, i.e. CCSD(T). The basic idea is to perform molecule-specific reparametrizations by fitting the semiempirical parameters to the available high-level 1D and 2D terms. Our automatic modeling scheme involves several aspects: (i) Modification of standard AM1 theory in order to allow for efficient, molecule-specific reparametrization. (ii) Implementation of analytical gradients of the total energy with respect to the semiempirical parameters. (iii) Use of a new global optimization scheme based on genetic algorithms for locating the most important minima at the 1D level. (iv) Local optimization of the global minimum at the 2D level.

All these features are implemented in the Molpro package of *ab initio* programs. Subsequently, vibrational frequencies and related properties can be computed by a VSCF program. First results showing the accuracy and timings of the new approach are provided.

[PI-14]

Tunable Hydrogen Bonds: Multi-Center Effects

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The proton affinity of Trichloroacetic acetate ion-4-Methyl-1H-imidazole anion has been used successfully to analyze the properties of the alpha-HB in the Trichloroacetic acetate ion-4-Methyl-1H-imidazole-Acetic acid anion as a function of the difference of the proton affinities of the two parts.

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[PI-15]

Coupled-Cluster Studies of the Photoisomerisation Reaction of Retinals

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The first few excited states of the 11-cis-retinal chromophore have been studied at the coupled-cluster approximative singles and doubles (CC2) level using triple- ζ quality basis sets augmented with double sets of polarisation functions. The two lowest vertical excitation energies of 2.14 and 3.21 eV [1] are in good agreement with recently reported experimental values of 2.03 and 3.18 eV obtained in molecular beam measurements [2]. Calculations at the time-dependent density functional theory (TDDFT) level using the B3LYP hybrid functional yielded vertical excitation energies of 2.34 and 3.10 eV for the two lowest states. Coupled-cluster optimisation of the molecular structure of the first excited yielded enhanced bond-length alternation of the retinal chain in the vicinity of the isomerisation center, whereas at the B3LYP level the largest increase in the bond-length alternation occurs at the β -ionone ring leading to a twist of the torsion angle at the β -ionone ring. The excited state structures obtained at the B3LYP and CC2 levels are very similar from C₉ to the Schiff base at N₁₆. Second-order Moller-Plesset (MP2) and CC2 calculations on retinal chromophore models also yielded qualitatively the same ground-state and excited state structures as obtained at the B3LYP DFT and TDDFT levels [3].

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[PI-16]

Hydrogen Fuel Production: Modeling Heterogeneous Catalysis From First Principles

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With the increasing international focus on carbon dioxide emissions and their contributions to global warming, there is considerable interest in hydrogen fuel. Steam methane reforming is one of the most important industrial processes for producing hydrogen fuel, and it allows for the capture and sequestration of carbon dioxide. Unfortunately the standard nickel catalyst deactivates relatively quickly due to carbon formation. We are developing the first, comprehensive mechanistic understanding of steam methane reforming on nickel catalysts using density functional theory. With this understanding, we can construct an ab initio kinetic model for the process and to identify key reaction steps that lead to catalyst deactivation. Quantum chemistry then allows us to virtually search for dopants that can resist carbon formation and extend the catalyst lifetime.

[PI-17]

Geometry and ^{27}Al Chemical Shift of Isolated Aluminum Atoms in the Framework of ZSM-5 Zeolite. A QM/MM and High Resolution ^{27}Al NMR Study

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Silicon rich zeolites (Si/Al ratio greater than 12) as ZSM-5, beta or MCM-22, represent important materials widely applied as catalysts and sorbents in the chemical industry. Their protonic forms are applied as acid catalysts in petrochemical processes, and moreover, their metal forms are employed as catalysts in environmentally important deNO_x reactions.

One of the most important properties of zeolites is the presence of aluminum atoms in the silicate framework. Silicon rich zeolites have a large number of individual framework T sites (24 in ZSM-5) which can be occupied by Al atoms. The Al siting in the zeolite framework significantly affects the nature and properties of acid sites as well as metal ions in extra framework positions and thus the accessibility as well as the local arrangement of both acidic and cationic catalytic centers. Therefore the knowledge of the Al siting is of crucial importance for both experimental and theoretical studies of catalysts based on silicon rich zeolites.

The Al siting and local geometry of AlO_4 tetrahedra in zeolite frameworks cannot be obtained by diffraction techniques due to a low framework Al content and a very similar electron density of Al and Si atoms. Nevertheless, framework Al atoms in zeolites can be studied using the high resolution ^{27}Al MAS NMR spectroscopy. However, theoretical modeling is essential for the interpretation of such NMR experiments.

In this contribution, we report the results of our combined theoretical (QMPOT) and experimental (^{27}Al 3Q MAS NMR) study investigating the siting of the Al atoms in the 24 distinguishable framework T sites of the ZSM-5 zeolite. A bare zeolite framework model (neither counter cations nor water molecules) was employed. Our calculations at the QMPOT(BLYP/TZP:zeolite force field) level allowed to interpret our ^{27}Al 3Q MAS NMR spectra of fully hydrated zeolites and to attribute some of the ^{27}Al resonances to the corresponding framework T sites. The calculated 24 values of ^{27}Al NMR isotropic chemical shift are in excellent agreement with the observed 13 ^{27}Al NMR isotropic shifts. The embedded cluster calculations also revealed the local geometry of the AlO_4 tetrahedra in the 24 T sites.

[PI-18]

Direct Location of the Minimum Point on Intersection Seams of Potential Energy Surfaces with Coupled-Cluster Methods

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The projected gradient technique for finding the minimum point on intersection seams of potential energy surfaces (PESs) was implemented for coupled-cluster and equation-of-motion methods within the Q-Chem electronic structure package. The examples of PES crossing minimization include nitrogen dioxide, trinitrogen, and the trinitrogen cation.

Analytic Derivatives for the Cholesky Representation of the Two-Electron Integrals**Francesco Aquilante, Thomas B. Pedersen, and Roland Lindh***Department of Theoretical Chemistry, Chemical Center, P.O.B. 124
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A critical issue for any *ab initio* or density functional theory (DFT) method which explicitly relies on the two-electron integrals is represented by the fact that increasing the number of basis functions per atom leads to a quartic scaling of the number of integral evaluations. The approach based on the Cholesky decomposition of the two-electron integral matrix² tackles this so-called “basis set quality problem” by exploiting the near and exact linear dependences in the product space of the atomic orbitals.

The use of this technique provides remarkably accurate results while greatly reduces the prefactor associated with the standard *ab initio* and DFT methods due to the fact the effective rank of the two-electron integral matrix is much smaller than the total number of atomic orbital distributions. Moreover, the accuracy of the approximation can be systematically improved by lowering the decomposition threshold. Nonetheless, the lack of an analytic formulation of the Cholesky vector derivatives has limited the spreading of this approach in the quantum chemistry community.

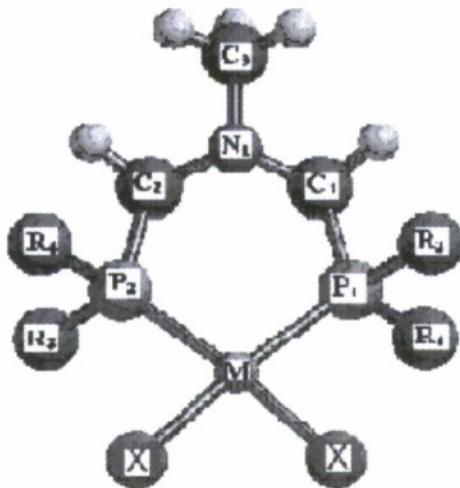
We show that with a suitable choice of auxiliary basis set, the Cholesky decomposition is equivalent to a density fitting (DF)/resolution of identity (RI) approximation² of the two-electron integrals in the coulombic metric. This complete unification of the two methods is exploited in order to propose a formalism for computing analytic gradients and higher derivatives of the Cholesky vectors.

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Comparison of Ni(II), Pd(II), Pt(II) Complexes of N,N-Bis(Dialkylphosphinomethyl)*Ahmet Koseoglu,^a Osman Serindag,^b Tereza Varnali^a^a Department of Chemistry, Bogazici University, Bebek, 34342 Istanbul, Turkey, e-mail: varnali@boun.edu.tr ^b Department of Chemistry, Cukurova University, 01330 Adana, Turkey

Phosphine ligands are known to stabilize complexes of transition metals and therefore play role in catalysis of organic reactions ie. hydrogenation and hydroformylation. N,N-bis(dialkylphosphinomethyl)aminomethane structures with alkyl = methyl, cyclohexyl, phenyl groups and their complexes with nickel (II), palladium (II) and platinum (II), X= Cl and I have been studied computationally making use of the DFT method. Structural changes and electronic distribution are compared.



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[PI-21]

Geometries of Transition-Metal Complexes from Density-Functional Theory

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A diverse set of 32 metal complexes from the first transition row has been identified, for which precise gas-phase geometries are known from electron diffraction or microwave spectroscopy experiments (50 symmetry-inequivalent metal-ligand bond distances in total). Several levels of density functional theory, i.e. various combinations of exchange-correlation functionals and basis sets, are assessed on the basis of their ability to reproduce these structural parameters, using mean and standard deviations of optimized vs. observed values as criterion. The ranking of some popular functionals, ordered according to decreasing standard deviation, is BLYP \approx HCTH $>$ B3LYP $>$ BP86 $>$ TPSS \approx TPSSh [1].

Vibrational corrections to the optimized equilibrium geometries almost exclusively increase bond lengths, and the corrections turn out to be highly transferable from one DFT level to the other [2]. For the whole test set, these vibrational corrections affect mainly the mean error, not the standard deviation of the error distribution. The recently introduced meta-GGA functional TPSS [3], together with its hybrid variant TPSSh, performs best of all tested functionals.

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[PI-22]

Are There Accurate DFT Treatments of Organic Energies?

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Increasing awareness that popular functionals fail to describe many energies accurately has ended expectations of black-box DFT usage. The performance of nine density functionals, compared by computing the bond separation reaction energies of 72 illustrative hydrocarbons with available experimental data, reveal that only Zhao and Truhlar's recently proposed M05-2X functional, with a 2.13 kcal/mol average deviation from experiment, performs satisfactorily. Isodesmic bond separation reaction energies further illustrate systematic underestimation of 1,3-alkyl-alkyl (protobranching) stabilization for *n*-alkanes, predominately due to inadequacies in assessing long and medium-range non-bonded attractive interactions.

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[PI-23]

**^{51}V NMR Chemical Shifts Calculated from
QM/MM Models of Vanadium Chloroperoxidase**

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^{51}V NMR chemical shifts calculated from QM/MM optimized models of vanadium dependent chloroperoxidase (VCPO) are presented. Starting from the known framework structure of the protein in the solid state, an extensive number of protonation states for the vanadium cofactor (active site) and a number of probable positional isomers for each of the protonation states are considered. The size of the QM region was increased incrementally to observe the convergence behavior of the ^{51}V NMR chemical shifts. The models are assessed based on comparison to experimental solid-state ^{51}V NMR results recently reported in the literature [1]. Isotropic chemical shifts are found to be a poor indicator of the protonation state, however, anisotropic chemical shifts and the nuclear quadrupole tensors appear to be sensitive to changes in the proton environment of the vanadium nuclei. The triply protonated (one axial water and one equatorial hydroxyl group) or a doubly protonated vanadate moiety in VCPO can be reconciled with the experimental solid-state MAS ^{51}V NMR data. These models were previously proposed as ground state models of VCPO based solely on energy [2,3]. The computation of the anisotropic ^{51}V NMR chemical shifts for QM/MM models of VCPO is therefore a useful tool for determining likely protonation states of the active site in VCPO. This is the first study to compute anisotropic NMR chemical shifts from QM/MM models of an active metalloprotein for direct comparison with solid-state MAS NMR data.

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[PI-24]

**Dipolar coupling constants: analysis of the hyperfine structure
in rotational spectra and determination of bond distances**

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The main interaction between the spins of two nuclei is the dipole-dipole coupling between their magnetic moments. The importance of these interactions lies in the facts that a) dipolar coupling constants should be considered for the proper analysis of the hyperfine structure in rotational spectra and b) that dipolar-coupling tensors provide an alternative way for determining bond distances. We compare computed dipolar coupling constants for small to medium-sized molecules to experiment, demonstrating the importance of including vibrational corrections for accurate predictions. In addition, we show how experimental dipolar coupling constants together with computed vibrational corrections can be used to derive equilibrium bond distances.

[PI-25]

**The Prediction of the Redox Enthalpy of Rubredoxin
from Accurate ab Initio Calculations**

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This poster describes a theoretical investigation into the electronic structure of the metalloprotein, rubredoxin, with a view to understanding the origin of its redox potential. Recent attempts to reproduce the redox potential from theory have highlighted the difficulties associated with accurately modelling the protein and solvent environments [1]. However, work on the redox thermodynamics of mutated forms of rubredoxin [2] suggests that the "...purely enthalpic term is driven by metal-ligand binding and by electrostatic interactions at the metal-protein interface..." Thus, accurate electronic structure methods may be capable of reproducing the redox enthalpy as a validation of theory before undertaking the detailed account of the solvent interactions required for an estimate of the entropy change. This work forms part of an on-going collaboration between the Computational Chemistry and Molecular Biophysics groups at Daresbury Laboratory, UK, on the subject of metalloproteins, and is a major user of the 2,500 processor computing resources (HPCx) at Daresbury.

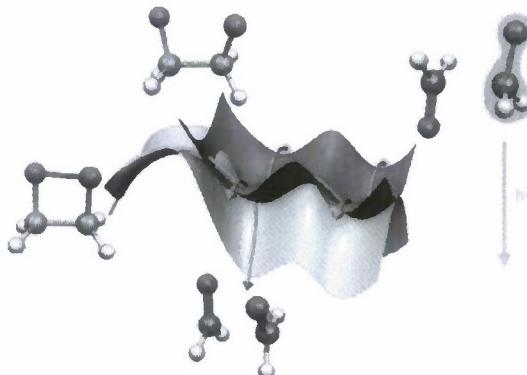
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The Chemiluminescence of 1,2-Dioxetane. Reaction Mechanism Uncovered

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The thermal decomposition of 1,2-dioxetane and the associated production of chemiluminescent products has been studied at the multi-state multi-configurational second order perturbation level of theory. This study is in qualitative and quantitative agreement with experimental observations with respect to the activation energy and the observed increase of triplet and singlet excited products as substituents are added to the parent molecule. The reaction mechanism of the chemiluminescence of 1,2-dioxetane is described to be due to a particular form of entropic trapping.



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Exploring the Full Conformational Potential Energy Surface of n-Pentane

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Chains of n-alkanes and n-alkyl groups are the simplest among the molecules with higher dimensional structures. Studying their conformational properties can then provide some help in solving the famous folding problems of proteins. Based on Hartree-Fock (HF) [1] and second-order Moller-Plesset (MP2) [2] computations, four rules were deduced for the sequences of the conformers of n-alkanes [3]. Furthermore, applying standard graph theoretical techniques a system of linear recurrence equations was deduced from the rules for the number of the possible conformers [4,5]. Within the Born-Oppenheimer approximation [6], the conformational potential energy (hyper)surface (CPES) of a molecule with n free torsional angles is a surface in the $(n+1)$ -dimensional space. The CPES can readily be obtained from the full PES (FPES) making the FPES stationary with respect to those internal coordinates which are not free torsional angles. The topology of the CPES determines the conformational properties of a molecule [7]. For the n-pentane molecule, CPES and FPES are two and forty-five variable functions, respectively. By quantum chemical computations at HF and MP2 levels of theory, every stationary point on the CPES of n-pentane was located. The usual Monte-Carlo and systematic (grid) search techniques afforded 11 (4) conformers (local minima), 20 (6) first-order saddle points (transition states) and 9 (4) local maxima. The numbers in parentheses are referring to the equivalence classes, *i.e.*, nonisomorphihc species. To determine all the stationary points, we scanned the CPES, and minimized, minimized-maximized as well as maximized the total molecular electronic energy with respect to the free torsional angles. All the reaction paths connecting the conformers to each other through the transition states were also determined. It can be concluded that there are fourteen unique stationary points on the CPES of n-pentane, while n-butane has only four.

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[Pl-28]

**Unravelling the Origin of Intermolecular Interactions
Using Absolutely Localized Molecular Orbitals**

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An energy decomposition analysis (EDA) method is proposed to isolate physically relevant components of the total intermolecular interaction energies such as the contribution from interacting “frozen monomer densities”, the energy lowering due to polarization of the densities and the further energy lowering due to charge transfer effects. This method is conceptually similar to existing EDA methods such as Morokuma analysis, but includes several important new features. The first is a fully self-consistent treatment of the energy lowering due to polarization, which is evaluated by a self-consistent field calculation in which the molecular orbital coefficients are constrained to be block-diagonal in the interacting molecules to prohibit charge transfer. The second new feature is the ability to separate forward and back-donation in the charge transfer energy term using a perturbative approximation starting from the optimized block-diagonal reference. The amount of charge transferred in each direction can also be calculated. Finally, the charge transfer energy in each direction can be represented in terms of one occupied orbital on a monomer donating electrons to a virtual orbital on another monomer. Unlike canonical monomer orbitals, this charge transfer occupied-virtual orbital pair is chemically significant. The newly proposed EDA method is used to understand the fundamental aspects of intermolecular interactions such as degree of covalency in the hydrogen bonding in water and the contributions of forward and back-donation in synergic bonding in metal complexes. Additionally, it is demonstrated that this method can be used to assist in solving practical chemical problems. The interaction of molecular hydrogen with open transition metal centers in potential hydrogen storage materials is one example, while study of the rhenium-alkane interaction with the goal to produce an isolable metal-alkane sigma-complex is a second example.

[Pl-29]

Ab Initio Simulation of Active Sites on Goethite Surfaces

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The aim of this work is to contribute to the understanding of the structure and properties of the goethite (α -FeOOH) surfaces by means of *ab initio* quantum chemical calculations using a cluster and periodic-boundary approaches. Investigated models contain three different surface hydroxyl groups -OH, μ -OH and μ_3 -OH. Energies of protonation, deprotonation and dehydroxylation of three different types of OH surface groups were calculated. The interaction energies of water molecules with different surface sites of neutral and defected models were obtained. It was found that the three structurally different hydroxyl groups on the goethite surface have very similar acidic properties while they differ by their proton affinity and dehydroxylation. The calculation of the interactions of water molecules with the goethite surface showed that the hydrogen bonds are responsible for the formation of the surface complexes with relatively large sorption energies.

[PI-30]

Reaction Mechanism of Direct Gas Phase Synthesis of H₂O₂ Catalyzed by Au₃
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The industrial production of propene oxide is a very important, but currently expensive and environmentally unfriendly process. It was discovered that gold nanoparticles supported on titanium silicates catalyze the epoxidation of propene by hydrogen peroxide species formed *in situ* from gaseous hydrogen and oxygen.¹ As a first step in understanding this complex mechanism, the formation of hydrogen peroxide from hydrogen and oxygen adsorbed on and activated by a Au₃ cluster is studied computationally. The reaction starts by adsorption and activation of O₂ on the Au₃ cluster and proceeds through formation of hydrogen peroxide radical leading to final product – hydrogen peroxide. All reactants, intermediates and product stay bound to the gold surface through out the course of the reaction. Geometry optimizations were done with the ZAPT method. The intrinsic reaction coordinate method was used to connect transition states with minima. Final energies are obtained using coupled cluster methods.

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The Role of Feshbach Resonances in Vibrational Relaxation of HF(V) by H Atoms

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Interest in the vibrational relaxation of HF(v) molecules by H atoms dates back to efforts to simulate the HF chemical laser [1]. Successful operation of a chemical laser requires that the pumping of excited HF vibrational levels be rapid with respect to the rates of collisional removal, either by direct inelastic, exchange inelastic or endothermic abstraction mechanisms. We describe fully three-dimensional quantum mechanical studies of H + H'F(v) quenching collisions on the *ab initio* Stark–Werner (SW) potential energy surface. A clear Feshbach resonance feature is observed in the calculated integral cross sections (ICS). By means of an adiabatic treatment, we can correlate the resonance peaks observed in the scattering calculation with metastable states trapped in the HF–H van der Waals well. This is confirmed by analysis of the probability density of this metastable state. Our investigation on the ICS as well as the relaxation rate constant resolves the discrepancy between the previous laser-induced fluorescence experiments and the classical trajectory calculations. It also provides motivation for the future search for experimental signatures of the role of resonances in HF vibrational relaxation.



References:

[1] P. H. Cornel and G. C. Pimentel, *J. Chem. Phys.* **49**, 1379 (1968).

[PI-32]

**High Quality Potential Energy Surfaces Based on Low Level
Normal Coordinates for Calculating Accurate Vibrational Spectra**

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In the context of VSCF and VCI calculations we have studied the influence of approximate normal coordinates for spanning high potential energy surfaces on vibrational frequencies. Normal coordinates obtained from a harmonic frequency analysis were used for spanning a multi-level 1D:CCSD(T)-2D:MP4(SDQ)-3D:MP2 potential:

$$V(q_1, q_2, \dots, q_{3N-6}) = \sum_i V_i(q_i) + \sum_{i < j} V_{ij}(q_i, q_j) + \sum_{i < j < k} V_{ijk}(q_i, q_j, q_k) + H.O.T. ,$$

CCSD(T) MP4(SDQ) MP2 neglected

We compare anharmonic frequencies obtained from multi level potential energy surface spanned by MP2 and DFT normal coordinates with corresponding values using CCSD(T) normal coordinates. Such benchmark calculations are provided for a test set of medium sized organic molecules. Mean absolute deviation with respect to the CCSD(T) reference calculations were found to be as low as 1–2 cm^{−1}. Furthermore, the generation of the normal modes at low computational levels lead to a significant speed-up of such calculations. Consequently, without introducing substantial errors this approximation allows for VSCF/VCI calculations on larger molecular systems.

[PI-33]

Scaling Reduced CCSD(T) and CCSDT(Q) Methods by Decomposition Schemes

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Accurate predictions by quantum chemical calculations, e.g., in thermochemistry require the use of highly correlated methods. Whereas CCSD(T) is the standard in this respect, quadruple excitations are needed if chemical accuracy is aimed at. This can efficiently be achieved through the use of a CCSDT(Q) code. The perturbative treatment of triples and quadruples respectively is the steepest scaling step in calculations that employ these methods. We present here schemes for scaling reduced CCSD(T) and CCSDT(Q) algorithms. As a starting point, a decomposition of the respective orbital energy denominators is utilised. In the case of the (T) correction, the obtained scaling behaviour with respect to the virtual orbitals requires an additional factorisation of the involved integrals. Such a procedure is not required in the (Q) case which should render this method numerically more stable than the decomposed (T) algorithm. The characteristics of the proposed schemes are discussed in this contribution and preliminary timings are given where available.

QM/MM Studies on Adsorption Complexes in Zeolites

Shampa Santra, Helena Komnik, Hermann Stoll, and Guntram Rauhut

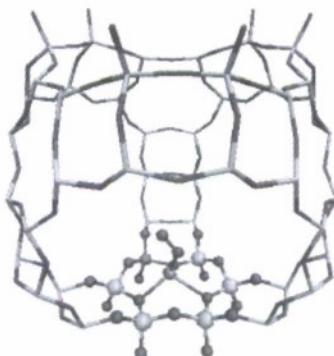
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High silica Cu-exchanged faujasite (Y type) zeolites can catalyze the oxidation of benzene with molecular oxygen. In order to study the catalytic activity of zeolites at the molecular level an accurate quantum chemical description of the system is mandatory. Therefore, hybrid quantum mechanics/molecular mechanics (QM/MM) calculations are used in which the active sites are calculated at the QM level whereas interatomic potential functions serve to describe the outer regions. Periodic boundary conditions are imposed.

The calculations are carried out with the QM-pot [1] program at the DFT level using triple- ζ quality basis sets. QM-pot (MOLPRO/GULP) models are used to describe the interaction of molecular oxygen with Cu(I) sites in faujasites. These calculations will be compared with results from QM calculations in which constraints are imposed in the geometry optimizations.

Different number of aluminium atoms have been introduced in the adsorption complexes and consequently charge neutralization is done by adding a corresponding number of protons. Selected parameters (bond lengths, bond angles) involving molecular oxygen and Cu in the adsorption complexes will be compared. Adsorption energies and vibrational frequencies are calculated at both QM/MM and QM level.

**References:**

[1] Sierka, M. and Sauer, J. *Faraday Discuss.* 1997, 106, 41.

[PI-35]

pK_a Values for Organocatalysts*

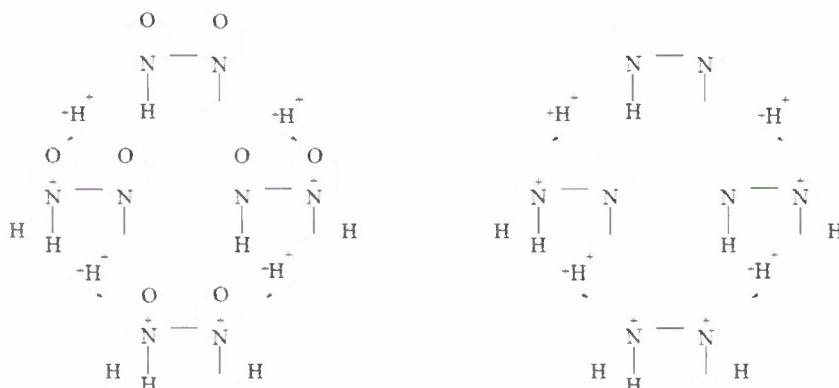
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Asymmetric catalysis represents one of the challenges in modern organic chemistry. However, the computational studies to understand asymmetric reactions involving organocatalysts are rare. The purpose of this work was to calculate the pK_a values of different derivates of bimorpholine and bipiperidine as the asymmetric organocatalytic reactions are pH-dependent. The study is being performed to explain the existing experimental results. Several catalysts have been used in aldol condensation reactions. The acidity of catalysts is important for getting better results in the stereoselective synthesis.

For calculations of the pK_a values using DFT methodology we have used four different protonation forms of derivates of bimorpholine and bipiperidine (see figure). Single proton can be transferred in two alternative ways.



This work helps to understand the experimental results. It was found that the derivates of bimorpholine have lower pK_a values than derivates of bipiperidine. The calculation of acidic properties of organic catalysts confirms results of synthesis— derivates of bimorpholine are better catalysts in the enantioselective cyclization reaction.

* This work was supported by Estonian Science Foundation grant no. 7135.

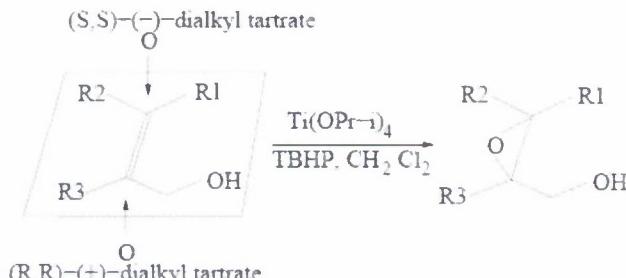
Modeling of Asymmetric Epoxidation of Cyclopentadiones

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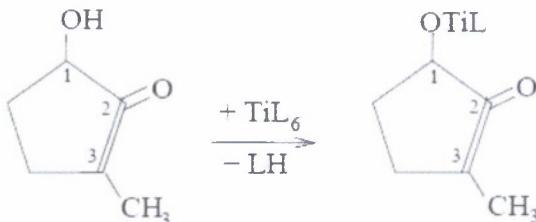
In 1980, Barry Sharpless showed that in the presence of *tert*-butyl hydroperoxide, titanium(IV) catalyst, and a chiral tartrate ligand, an allylic alcohol can be converted into epoxides with good yield and with excellent enantioselectivity. This reaction is now referred to as the Sharpless epoxidation.



The reaction has been improved to give excellent results for almost all types of allylic alcohols except for a few special cases. Especially for five-membered ring as the substrate the reaction mechanism is not known in detail.

In this work we modeled epoxidation of 3-methyl-1,2-cyclopentadione in the presence of a chiral titanium tartrate complex (Sharpless catalyst). The five-membered ring makes it harder to adapt to the required conformation of the transition state of the catalytic reaction than the more flexible allylic alcohols.

We studied the mechanism of epoxidation reaction that occurs between a double bond of the cyclopentadione and *tert*-butylperoxide bound to the titanium center in the tartrate ligand. Density-functional theory was used. The transition state at BP86 level with SV(P) basis was modeled using the Turbomole software. It was assumed that substrate binds to the catalyst via the oxygen at carbon 1.



We shall present detailed results of the reaction mechanism. Usually this reaction is studied based on the assumption that the substrate and oxidizer are both bound to the same titanium atom, but we used also a model where the substrate and oxidizer are on different titanium atoms.

[Pl-37]

Towards Experimental Observation of Quartet States of Ozone Cation: Insights from Coupled Cluster Theory

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Ozone plays a vital part in our stratosphere by absorbing ultraviolet radiation. Little is known about the quartet states of the ozone cation which may play an important role in its chemical reactions. Open shell Coupled Cluster theory [UCCSD and UCCSD(T)] with Dunning's correlation consistent polarized core valence basis sets (cc-pCVXZ, X = T, Q, and 5) is being used to examine the low-lying excited electronic states geometry and excitation energy from the ozone ground state. At the UCCSD(T) cc-pCV5Z level of theory, $^4A_1 O_3^+$ lies lowest in energy followed by 4A_2 , 4B_2 , and 4B_1 at 0.18, 0.53, and 3.14 eV, respectively. Adiabatic excitation energies from the $X^1A_1 O_3$ are 13.61, 13.79, and 14.14 eV for $^4A_1 O_3^+$, $^4A_2 O_3^+$, and $^4B_2 O_3^+$, respectively. It has been suggested that the most viable pathway to the quartet states would be to ionize from the triplet neutral state. The UCCSD(T) cc-pCV5Z level of theory predicts a degenerate triplet ground state for ozone, 3A_2 and 3B_2 , while 3B_1 and 3A_1 states lie 0.26 and 3.32 eV higher in energy, respectively. Starting from $X^1A_1 O_3$, excite an electron to the 3B_2 state (1.26 eV above), then ionize this triplet to one of the quartet cation states; 12.35, 12.53, and 12.88 eV for $^4A_1 O_3^+$, $^4A_2 O_3^+$, and $^4B_2 O_3^+$, respectively. Current work focuses on extending our computations to higher order coupled cluster theory, vertical excitation energies, and vibrational frequencies at the higher levels of theory.

[Pl-38]

Variational Vibrational Calculations in Normal Coordinates with Arbitrary Potentials

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A new, effective and general algorithm is suggested for exact variational vibrational calculations of N -atomic molecules using normal coordinates. The protocol has three essential parts. First, the Watson Hamiltonians (of nonlinear or linear reference configuration) are applied, which have a universal form. Second, a high accuracy potential or force field can be used in the calculations with the help of an exact, analytical transformation formula from normal to internal coordinates (e.g., bond lengths, bond angles, etc.). Third, the matrix of the Watson Hamiltonians is constructed in a discrete variable representation in which the matrix of the potential energy operator is always diagonal, whatever complicated the potential function is, and the matrix of the kinetic energy operator is a sparse matrix of special structure. Details of the suggested algorithm as well as results obtained for small molecular systems are presented.

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- [1] J. K. G. Watson, Mol. Phys. 15, 479 (1968).
- [2] J. K. G. Watson, Mol. Phys. 19, 465 (1970).

Toward First-Principles Complete Spectroscopy of Small Molecules

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During the last decades several numerical algorithms have been developed for the computation of high-accuracy rovibrational spectra of small molecules. Grid methods, in particular the discrete variable representation (DVR) technique, are particularly advantageous for setting up the matrix representation of the Hamiltonian needed to solve the (ro)vibrational Schrödinger equation with arbitrary precision. Treating the singularities present in the (ro)vibrational Hamiltonian in internal coordinates is important for computing complete spectra of molecules [1]. Simple strategies for solving the nuclear motion problem of triatomic molecules are introduced [2]. In particular, solution strategies are given for treating all the important singularities in a triatomic (ro)vibrational Hamiltonian using a suitable nondirect-product basis [1] and utilizing an efficient finite basis representation [3]. The newly developed program packages are described. These packages have been employed for computing (ro)vibrational energy levels for several molecules, such as H₂O, CO₂, N₂O, CH₂, CCl₂, CHCl, and H₃⁺. The equilibrium and temperature-dependent effective structures of the water molecule are given and compared to experiment.

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[PI-40]

Composite CCSDT(Q) Investigation of the Ketenyl Radical HCCO and Its Barrier to Linearity

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The troublesome barrier to linearity of the combustion intermediate ketenyl radical (HCCO) has been computed via focal point extrapolation through coupled cluster theory with single, double, triple, and perturbative quadruple excitations [CCSDT(Q)], utilizing the aug-cc-pVXZ ($X = D, T, Q, 5, 6$) family of basis sets. Previous theoretical treatments of HCCO have shown a very strong dependence on the correlation level and basis set employed, particularly for the CCH bond angle, leading us to define a composite approximation to all-electron CCSDT(Q)/aug-cc-pCVQZ, which is formulated within the spirit of the focal point approach. After optimizing the geometries of all species at the CCSDT(Q)-AE/aug-cc-pCVQZ level of theory, we further refine the energetics and monitor the performance of the composite approach by performing a full focal point analysis to account for basis set error. Auxiliary corrections such as diagonal Born–Oppenheimer corrections and relativistic effects to the barrier to linearity are included. Additionally, we compute fundamental vibrational frequencies by correcting aug-cc-pVQZ CCSD(T) harmonic frequencies with anharmonicities derived from CCSD(T)/cc-pVTZ. The resulting (v_2, v_5) of (2017, 478) cm^{-1} agree very well with the experimentally derived values, (2023, 494) cm^{-1} .

[PI-41]

New Parallel Algorithm for MP2 Energy and Gradient Calculations

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Second-order Moller–Plesset perturbation theory (MP2) is one of the most important methods in quantum chemistry. MP2 can treat the dispersive component of non-covalent interactions which generally used density functional theory (DFT) cannot describe. A new parallel algorithm for MP2 energy [1] and gradient [2] calculations has been developed by introducing a two-step integral transformation and implemented into the quantum chemistry program GAMESS. In the two-step transformation, atomic orbital (AO) indices are distributed from the AO integral generation to the third quarter transformation and molecular orbital indices are distributed from the fourth transformation to the MP2 energy calculation. Test calculations are performed on taxol ($\text{C}_{47}\text{H}_{51}\text{NO}_{14}$) with 6-31G(d) and 6-311G(d,p) basis sets (1032 and 1484 basis functions) and luciferin ($\text{C}_{11}\text{H}_{8}\text{N}_2\text{O}_3\text{S}_2$) with aug-cc-pVDZ and aug-cc-pVTZ (530 and 1198 basis functions) using up to 32 CPUs. The results demonstrate the high parallel efficiency of the program.

References:

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[PI-42]

Global fit of potential energy surfaces involved in the C + OH reaction

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To some extent the simplest radical-radical reactions are those in which one atom is transferred from a diatomic radical to an atomic radical. Among these, reactions involving C, N and O atoms and oxidizing radicals such as OH are likely to play a major role in the interstellar medium and in atmospheric and combustion chemistry. However they are characterized by the existence of multiple potential energy surfaces (PES) (12 states for the C(³P) + OH(²Π) interaction). In general, the lowest PES decreases monotonically as the radicals approach and unpaired electrons on each radical pair up to form a chemical bond. Consequently, the first stage of radical-radical reactions is often the formation of an internally energized complex.

While the rate constants for the O + OH and N + OH reactions have been obtained from experiments in the 40-300 K temperature range[1], only upper limits for the rate constant of the C + OH collision have been published [2,3]. Indeed, experimental studies are difficult for reactions between pairs of free radicals especially when the two radicals are not of the same species. This has motivated the present theoretical study.

So we have built up three-dimensional potential energy surfaces for the ground state X²A' leading to the CO(X¹Σ⁺) + H products[4] and for the first two doublet states dissociating into CO(a³Π) + H. Analytical fits of these PESs as well as their derivatives have been considered in order to include them in dynamical treatments [5].

References:

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[PI-43]

High-Order Corrections to the Rotational Constants by Vibrational-Rotational Perturbation Theory

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Expressions for the second-order rotation-vibration interaction constants of polyatomic molecules, γ_{ij}^α , determined by vibrational-rotational perturbation theory are presented. Results for some polyatomic molecules are included and analyzed.

[Pl-44]

Harmonic Vibrational Frequency Scaling Factors for the New NDDO Hamiltonians RM1 and PM6

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Scaling factors have been derived for obtaining fundamental vibrational frequencies with the recently introduced semiempirical methods RM1 and PM6, are implemented in MOPAC2007[1]. A least-squares approach is used with a training set comprised of 531 singlet-state molecules and 1577 distinct vibrations, extracted from the NIST Computational Chemistry Comparison and Benchmark Database (CCCBDB). Results are presented both for the conventional single-factor fitting, and for multi-factor models designed to incorporate different anharmonicity effects for various types of normal modes. The new NDDO methods along with the multi-linear fitting are shown to provide improved prediction of vibrational frequencies.

References:

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[PI-45]

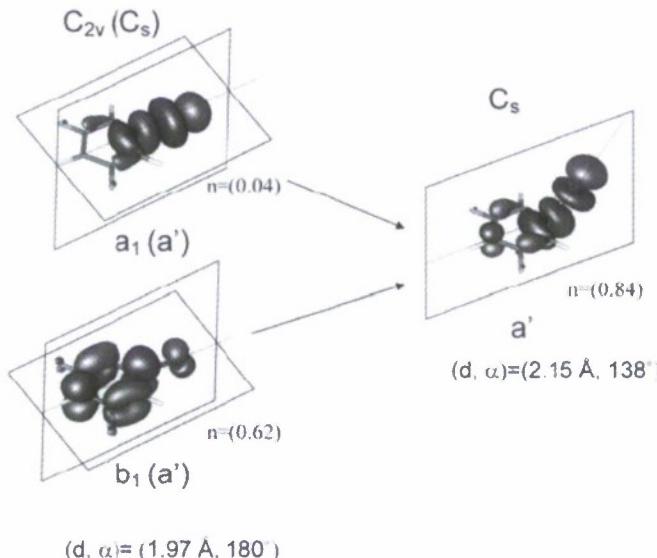
Low-Energetic Excited State Dynamics of Halogenated Benzenes

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For several years, low-energetic photodissociation of halogenated aryls has been investigated by means of femtosecond pump-probe measurements. At this timescale, nuclear motions in molecules can be followed and ultimately the outcome of chemical reactions can be controlled. The experimental techniques in this area are well developed, but even a qualitative understanding of the results requires detailed theoretical information. Quantum chemistry was therefore introduced at an early stage to identify the electronic states involved, and thereby find the reaction mechanism. Still, the large number of states involved, and the presumptive importance of including non-adiabatic coupling in the model for long prevented more elaborate theoretical investigations.

In this project, the recently improved and extended *ab initio* MS-CASPT2/CASSCF and CASSI methods in conjunction with quantum dynamics simulations are used to interpret femtosecond laser measurements of the dissociation of halogenated benzenes. Thereby, it has been established that the dissociation mechanism corresponds to a transition from a bound $^1\pi\pi^*$ state to a spin-mixed $\pi\sigma^*$ or $\sigma\sigma^*$ state. Further, the geometrical changes accompanying this electronic transition have been identified and an explanation based upon molecular orbital mixing to the mechanism has been found.



Orbital mixing in the photodissociation of bromo-3,5-difluorobenzene.

References:

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[Pl-46]

Recent Advances in Explicitly Correlated Local MP2 Theory

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Based on the complementary auxiliary basis set (CABS) approach results obtained within a general orbital-invariant formulation of the MP2-F12 method [1,2,3] are presented. New approximations 3B and 3C are proposed. If the generalized Brillouin condition (GBC) is assumed, the approximation 3B becomes equivalent to approximation 2B of Klopper and Samson [4]. The new method 3C is computationally significantly cheaper than 3B but yields virtually identical results. The accuracy of the methods is demonstrated for reaction energies of 16 reactions involving 21 molecules. Local approximations lead to low-order scaling without significant loss of accuracy. The usefulness of diagonal approximations is discussed. Nearly linear scaling with molecular size has recently been achieved in DF-LMP2-F12/2*A(diag) theory. Using appropriate prescreening techniques the evaluation of the 3-index integrals involving the short range correlation factor $e^{-\beta r_{12}}$ scales linearly with molecular size. Just the Coulomb integrals still scale quadratically, but this does not affect much the overall linear scaling because the total time spent in Coulomb integral evaluation is minor.

References:

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[Pl-47]

MARVEL: Measured Active Rotational-Vibrational Energy Levels

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MARVEL is a protocol and a computer code which can be used to determine experimental rotational – vibrational energy levels from the measured transitions using a weighted least-squares inversion process. The MARVEL protocol can be summarized as follows: (a) collect, evaluate, select, and compile all available measured transitions (with proper assignments and uncertainties); (b) determine all spectroscopic networks (SN) (including floating SNs, and orphans); (c) use a weighted least-squares-type procedure to obtain the energy levels and associated uncertainties; (d) improve the uncertainties of the transitions while MARVEL results in a self-consistent set of energy levels and transitions. MARVEL levels are active in the sense that if new experimental transitions become available new, energy levels can be obtained with improved uncertainties. The code was tested on the H_2^{17}O isotopologue of water. MARVEL has also been used to test the interval accuracy of high-resolution spectroscopic measurements of water isotopologues.

[PI-48]

Electrostatic versus Non-Electrostatic Effects in DNA

Sequence Discrimination by Divalent Ions Mg(II) and Mn(II)

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Mg(II) and Mn(II) ions are critical to the functioning of phosphoryl transfer enzymes, such as restriction endonucleases. Although playing similar roles in the chemical steps, these ions govern substrate specificity via modulating sequence discrimination by up to a factor of 10^5 with Mg(II) and only up to a factor of 10 with Mn(II). To explain whether such diversity originates in fundamental differences in the electronic structures of the nucleobase – hydrated metal ion complexes, structures and interaction energies were determined at the density functional (DFT) and second order Moller–Plesset (MP2) levels of theory. Although both metal ions favor identical binding sites, Mn(II) complexes exhibit greater distortions from the ideal octahedral geometry and larger variability than the corresponding Mg(II) systems. In inner-shell complexes, with direct contact between the metal and the nucleobase, Mg(II) is preferred over Mn(II) in the gas phase, due primarily to *non-electrostatic* effects. The interaction energies of the two metal ions are more similar in the outer-shell complexes, likely due to reduced charge transfer between the hydrated metal ion and base moieties. Inclusion of solvation effects can amplify the relative nucleobase preferences of Mg(II) and Mn(II), indicating that bulk hydration modulates the balance between electrostatic and *non-electrostatic* terms. In most cases the base substitutions in solution are more facilitated by Mn(II) than by Mg(II). Electrostatic properties of the environment were demonstrated to have a major influence on the nucleobase preferences of the two metal ions. Overall, quantum chemical calculations suggest that the contrasting selectivity of Mg(II) and Mn(II) cofactors towards nucleobases derives from the larger flexibility of the Mn(II) complexes accompanied by the excessive polarization and charge transfer effects as well as less favorable solvation.

[PI-49]

Manganese Complexes for Artificial Photosynthesis

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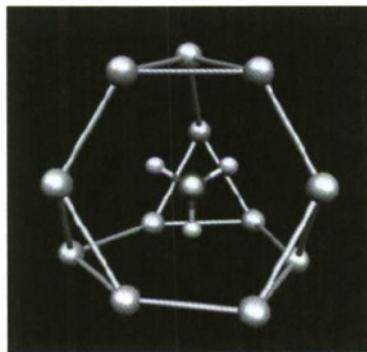
There is a strong international interest in the development of artificial photosynthesis, but to reach it great research efforts have to be done, including concerted work from different fields. Scientists aim to design a molecular system to mimic the most important energy-converting process in biosphere, natural photosynthesis, using solar energy for direct fuel production. There, ruthenium dyes are used as „antenna molecules”, to initiate photoinduced electron transfer (ET) involving complex manganese-containing molecules as acceptors. Sometimes the products are short-lived radical intermediates and the present understanding of these electron transfer reactions, is much poorer than in solution. Theoretical work is therefore needed to understand them in detail, since the complexity of these ET systems in the past has largely prevented accurate, quantum-chemical, calculations to formulate increasingly realistic models. Besides the calculation of molecular structures, the computation of spectroscopic parameters obtained by various techniques is of increasing interest. With that in mind, we address the magnetic resonance parameters of the dimanganese part of the complex in its superoxidised antiferromagnetically coupled Mn(III)Mn(IV) states.

Criminal Applications of Quantum Mechanics: Putting Molecules Behind Nano-Bars
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A novel type of core-shell clusters, with a molecule encapsulated in and interacting non-covalently with a metal cluster cage, is exemplified by a methane core in a 12-atom gold shell, $\text{CH}_4@\text{Au}_{12}$. The system has a closed-shell metastable state, with a considerable barrier (≈ 2 eV) to escape of the molecule from the cage. This exhibits such cages as potential nanocapsules (nano-vessels) for storage and transportation of molecular loads.

The metal shell acquires shape matching that of the molecule and differing from the shapes of pure gold cluster, Au_{13} , and of analogous C_5Au_{12} cluster with an open-shell radical core [1]. This suggests a possibility of flexibly designing metal cluster-cage structures by inserting proper molecular fillers. The interaction energy in $\text{CH}_4@\text{Au}_{12}$ is dominated by attractions between the shell atoms, while the core mainly “inflates” the shell via a relatively weak repulsion.



Ionization and electronic (spin) excitation reduce the system stability, leading to breaking the cage and releasing the molecule. This could be used for a controlled release of the molecular load. Moreover, the moderate singlet-triplet gap of ≈ 0.6 eV suggests an appreciable chemical reactivity of the neutral species, with some reactions likely to free the molecule from the cage which could then serve as a catalytic agent (gold cluster).

Electronic excitation energy, vertical ionization energy (VIE) and electron affinity (VEA) of $\text{CH}_4@\text{Au}_{12}$ reproduce those of the empty (geometry-frozen) Au_{12} shell, reflecting the excitation and charge localization in it. This could allow creation of molecule-inflated cluster-cages with designed unique electron-donor/-acceptor properties. Insertion of methane into the gold cluster affects these properties selectively, by increasing VIE while preserving VEA. Such variations are quite different from those for the C_5 radical core [1], potentially allowing a more flexible design of the electronic properties of metal clusters by molecular doping.

The $\text{CH}_4@\text{Au}_{12}$ and similar clusters could be produced in experiments by laser evaporation of metal (Au) in the atmosphere of molecules of interest (CH_4). Detection can be facilitated by their spectral signatures including red-shifted, degeneracy-lifted and intensity-reduced vibrations of the molecular core.

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[Pl-51]

**A Surface-Hopping Simulation of the Photodynamics
of the all-trans-Pentadieniminium Cation**

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The pentadieniminium-cation is a partial model for Retinal in Bacteriorhodopsin, the central chromophore in the active center of the light-sensitive protein. Absorption of light by the chromophore results in fast, selective and radiationless isomerisation and deactivation of the excited state, thus initiating proton pumps in cellular membranes. The theoretical modeling of the dynamics of this biological light-reaction proves to be quite difficult as both, the calculation of energy-hypersurfaces of electronically excited state and especially of their conical intersections is computationally very demanding. These conical intersections act as funnels, facilitating the fast radiationless deactivation of excited states. The nonadiabatic dynamics of Retinal based on adequate multireference methods will not be possible in the near future, but the simulation of smaller, partial systems can give us a good indication of how the entire molecule will react upon electronic excitation and shows, which way to proceed in the development of calculation and programming techniques. The simulations were carried out with the NEWTON-X program using the Columbus package of programs to obtain the analytical MRCI-gradients and nonadiabatic coupling vectors. NEWTON-X uses Tully's fewest switches algorithm for on-the-fly surface hopping dynamics. After a methodical exploration, the most extended calculations were performed on a MRCIS(4,5) level based on SA-2-CASSCF(6,6) orbitals with a 3-21G* basis set. Additional dynamics calculations were performed with the TDDFT and RICC2 methods, but failed to describe even the initial phases of the photodynamical process. It could be shown, that after excitation a clear sequence of events occurs including the development of a biradical structure, averaging of the double and single bond lengths and subsequent torsion around the 2-3 double bond. The lifetime of the excited state (149 fs) and the geometry for the funnel to the ground state were determined.

[Pl-52]

**Analytic Calculation of the Diagonal Born–Oppenheimer Correction
within Coupled-Cluster Theory**

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Schemes for the analytic calculation of the diagonal Born–Oppenheimer correction (DBOC) are formulated and implemented for use with general single-reference configuration-interaction (CI) and coupled-cluster (CC) wave function models. To reduce the computational effort of the CC calculation of DBOC, a perturbational approach has also been developed. Calculations are reported to demonstrate the convergence of the DBOC with respect to electron-correlation treatment and basis set as well as to investigate the accuracy of the perturbational approach. The importance of electron-correlation contributions to the DBOC is illustrated with the computation of atomization energies of small to middle size systems.

[PI-53]

Dual-Basis Methods for Electronic Structure Theory

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The expansion of a wavefunction in a finite atomic orbital basis forms one of the most common approximations in electronic structure theory. The extent of this approximation can have drastic implications on the quality of results—sometimes as large as the choice of the method itself. Large basis set results are thus desirable but come at considerably higher cost. Self-Consistent Field (SCF) calculations, for example, scale nearly linearly with respect to system size but quartically with respect to basis set size; the intrinsic non-amenableability of large basis sets to linear scaling algorithms further complicates matters. The Dual-Basis (DB) method provides a means of capturing these basis set effects at significantly reduced cost. An iterative SCF calculation is performed to convergence in a small subset of the larger, target basis; subsequently, a perturbative correction is applied in the large basis set (amounting to an approximate Roothaan step) to account for remaining basis set effects. Cost savings stem from the non-iterative large-basis SCF, as well as integral screening in the large basis. The DB formalism has been applied to HF, DFT, and MP2 energies and gradients, with triple- and quadruple-zeta basis sets. Errors in bond breaking energies are only 0.08 kcal/mol (MP2) and 0.03 kcal/mol (B3LYP), with roughly a factor-of-10 speedup in calculation time. Nuclear force calculations exhibit speedups of 50-75%, with structure errors less than 0.001 Å. The small basis/large molecule regime has also been shown to benefit from our formalism. A newly constructed 6-4G minimal basis set serves as the small basis pairing for 6-31G*. The same time savings are now seen in this commonly used regime, with suitably acceptable errors in energies, molecular structures, and frequencies. Application to non-covalent interactions in large systems, including fullerenes, has now been made feasible, using DB-DFT and DB-RI-MP2.

[PI-54]

Relativistic Effects on Molecular Geometries Using Direct Perturbation Theory

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An analytic scheme for the computation of energy gradients (i.e. forces) including relativistic corrections via Direct Perturbation theory (DPT) is presented. Since the relativistic treatment within DPT corresponds to the calculation of first derivatives of the energy, the corresponding corrections to the nuclear forces require the use of second-derivative techniques, such as those, for example, available in the ACESII program package for Hartree-Fock (HF), second-order Moller-Plesset (MP2) perturbation theory, and various coupled-cluster (CC) methods. For a selected set of molecules containing first- and second-row elements (i.e. HF, HCl, H₂O and H₂S), relativistic effects on geometrical parameters are investigated with an emphasis on basis-set convergence, additivity of electron correlation and relativity, as well as the importance of relativistic effects in high-accuracy predictions of equilibrium geometries.

[PI-55]

Comparison of Algorithms for Conical Intersection Optimisation Using Semiempirical Methods

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Intersections of potential energy surfaces (conical intersections) play a crucial part in many photochemical reactions. Conical intersections in polyatomic systems form a multi-dimensional scan, which can be characterised by finding the minimum energy crossing point using constrained optimisation techniques. Several algorithms have been developed for optimising conical intersections, including a penalty function method [1], a projected gradient method [2-4], and a Lagrange multiplier method [5,6]. The penalty function method requires only the energies and gradients of the states involved, whereas the other two methods require the calculation of non-adiabatic coupling terms [7]. We have implemented the three algorithms in a development version of the semiempirical MNDO program. Their performance is measured against a set of well-known small molecule conical intersections. The Lagrange-Newton method is found to be the most efficient, with the projected gradient method also competitive. The penalty function method can only be recommended for situations where non-adiabatic coupling terms cannot be calculated.

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[PI-56]

The CCP1GUI Computational Chemistry Graphical Interface

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The CCP1GUI project has arisen as a result of demand within the UK academic community (principally through CCP1) for a free, extensible Graphical User Interface (GUI) for community codes, particularly for teaching purposes. The CCP1GUI is designed to present a uniform interface to a range of different codes, allowing users to run calculations (both locally and on remote/Grid resources) and visualise the results from within the same environment. The CCP1GUI has been built around the Python open-source programming language (www.python.org) and the VTK visualisation toolkit (www.vtk.org), both of which have been ported to all the major operating system platforms (Mac, Linux, Windows, Solaris, AIX, etc.). The CCP1GUI is therefore capable of running on all of these systems. Interfaces to GAMESS-UK, Dalton, Molpro, Chemshell and MOPAC have already been developed and other interfaces are being developed as requested.

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[Pl-57]

Magnetic Resonance Properties of $^{129/131}\text{Xe}$ in Xe@C_{60} Beyond the Non-Relativistic Approximation. Electron Correlation, Relativistic Effects, Solvent Effects and Role of the Dynamics

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Xe atom is an excellent magnetic resonance (MR) probe. Its inertness together with high sensitivity of its MR parameters to the local surroundings allows for probing of material properties and processes via $^{129/131}\text{Xe}$ NMR techniques. The MR sensitivity of Xe atom is intrinsically given by its large and polarizable electron cloud. Xe@C_{60} serves as a good computational model for validation of methodology for studies of Xe atom confined inside a cavity/material. It is a relatively small and symmetric system with clearly confined Xe atom.

We systematically investigate the role of various physical contributions to the $^{129/131}\text{Xe}$ chemical shift and the ^{131}Xe nuclear quadrupole coupling in Xe@C_{60} . We validate the density functional approach wrt accurate ab initio methods [up to CCSD(T)] for calculations of MR properties, using a small, computationally efficient model, $\text{Xe...C}_6\text{H}_6$. The $\text{Xe...C}_6\text{H}_6$ calibration allows for choosing reasonable basis set and good-performing density functional for calculations of the large Xe@C_{60} system. We further evaluate the relativistic effects using the Breit-Pauli Perturbation Theory. The influence solvent effects and the Xe dynamics on $^{129/131}\text{Xe}$ MR properties are investigated in more detail. If finalized by the time the conference takes place, the study on the influence of the cage dynamics on Xe shift will be also presented.

[Pl-58]

Multireference Coupled Cluster Theory: Derivation of Coupling Terms and a New Implementation of MkCC BWCC and apBWCC

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We have recently derived closed expressions of the coupling terms that arise in Mukherjee's [1] state-specific multireference coupled cluster (MkCC) and implemented them in PSIMRCC, a new coupled cluster computer code developed at University of Georgia, interfaced to PSI version 3.2.3 [2]. Our code is also capable of performing Brillouin-Wigner [3] multireference coupled cluster (BWCC) computations, together with the a posteriori size-extensivity correction (apBWCC) [4,5]. These state-specific theories aim at computing one electronic state at a time and are not affected by intruder states. Therefore, they represent the most promising methods to study diradicals, bond breaking, and excited states, within a rigorous multireference coupled cluster formalism. Development of this code was aided by our string-based code (DETC++), capable of computing arbitrary order multireference coupled cluster wavefunctions [6]. In this poster we report applications of MkCCSD to a series of relevant chemical problems that require a multireference zeroth order wavefunction. Furthermore, we will present preliminary results on the effect of the inclusion of approximate iterative triple excitations.

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Binding Sites of Water to the Guanine - Cytosine Cation - Radical Base Pair

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The interaction between the guanine-cytosine cation-radical base pair and one water molecule leads to no fewer than ten local minima. All but one of the equilibrium structures arise from the dipole moment of water pointing toward the base pair cation. Water molecules that bind directly to guanine interact more strongly than those that bind directly to cytosine due to the localization of positive charge on guanine. At each binding site, nuclear repulsion and electrostatics compete to determine whether the plane of water is parallel or perpendicular to the plane of the base pair. The water molecule also acts as an electron donor to the singly-occupied, electron-deficient guanine molecular orbital. In the corresponding equilibrium structure, water sits directly above guanine with the oxygen atom pointing toward the pi-system. The binding sites of water to the guanine-cytosine cation drastically differ from binding sites of water to the neutral species. Density functional (B3LYP) theory with a DZP++, double-zeta plus polarization and diffuse functions, basis set were used to carry out all computations on the guanine-cytosine radical cation and water cluster.

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**Theoretical Study on the Structures and the Binding Energies
of B_nH_n , B_nH_{n+1} , B_nH_{n+2} ($n = 3\sim6$) Complexes**

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The structures, vibrational frequencies and dissociation energies of hydrogen-boron complexes, B_nH_n , B_nH_{n+1} and B_nH_{n+2} ($n = 3\sim6$) have been investigated at the B3LYP/6-311G** level of theory. The global minima for the most hydrogen-boron complexes have a closed three center B-B-B bond, and hydrogen bridged three center bonding also plays an important role in the stability of the isomers. The dissociation energies for B_nH_n , B_nH_{n+1} and B_nH_{n+2} ($n = 3\sim6$) complexes have been predicted, and zero-point vibrational energies (ZPVEs) are considered to compare with experimental results.

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[PI-61]

Structures and Stabilizations of Copper-Water Complex

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Theoretical calculations were carried out to investigate structures and stabilizations of copper-water complexes. The possible structures of $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ for $n = 1-8$ were geometry optimized at HF/6-31G(d,p) level and their energies were more accurately determined at MP2/6-31G(d,p) and B3LYP/6-31G(d,p) level of theory. In addition, for $n = 6, 7$, and 8 , single point calculations using MP2/6-31++G(d,p), MP2/6-311G(d,p) and MP2/6-311G(2df,p) were also performed. Our investigation revealed that for $n = 6, 7$, and 8 only 5-fold and 6-fold coordination complexes are observed in the first solvation shell. The 5-fold coordination complex consists of square pyramidal-like (spy) and trigonal bipyramidal-like (tbp) structures whereas the 6-fold is the distorted octahedral (oct) structure. For $n = 6$, at 6-31G(d,p) basis all methods predicted tbp as the most stable form (4.11 kcal/mol lower than oct at MP2 level). However, at MP2/6-311G(d,p) and MP2/6-311G(2df,p), the oct becomes more stable by 1.81 and 1.41 kcal/mol respectively. For $n = 7$ and $n = 8$ all methods and basis sets agree that tbp is more stable and the oct lies slightly above tbp structure. Thus, oct and tbp structures could co-exist in solution but tbp is more abundant in agreement with the recent neutron diffraction experiments [1].

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[PI-62]

Faster DFT with mrXC

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A new algorithm, which speeds up DFT exchange-correlation numerical integration by 5-7 times with no loss of accuracy, will be presented. The new method, called multiresolution exchange-correlation (mrXC), takes advantage of the variation in resolution among the Gaussian basis functions, and shifts the calculation associated with low-resolution (smooth) basis function pairs to an even-spaced cubic grid. MrXC does not alter the formulism of the current standard algorithm based on the atom-centered grid (ACG), but instead employs two fast and accurate transformations between the ACG and the cubic grid. Improving the efficiency of exchange-correlation integration has become necessary, especially with the new Fourier Transform Coulomb method pioneered by Dr. Pulay's group. The implementation of mrXC with local density approximation has been published. In this conference, we will present the results of the implementation with GGA-type functionals in Q-Chem program, which requires additional algorithmic design.

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[PI-63]

**An Efficient Implementation of the Analytical Gradient of
Dual-Basis Resolution-of-the-Identity Second-Order Moller-Plesset**

Perturbation Theory with Application to the Benzene Dimer

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In this work, we present the analytical gradient of dual-basis second-order Moller-Plesset perturbation theory within the resolution-of-the-identity approximation (DB-RI-MP2). Interestingly, analytical gradient theory within the DB-RI-MP2 model involves significant changes to both the theory and computation of the coupled-perturbed self-consistent field equations (CPSCF). From a theoretical point of view, the number of orbital responses required in DB-RI-MP2 analytical gradient theory has been reduced to the product of the number of occupied and virtual orbitals determined by the rank of the small, or subset, atomic orbital basis. Such a reduction in the number of variables required for linear response theory represents a marked and formal change in analytical gradient theory and will apply to any correlation method that is based on the DB wavefunction. From a computational point of view, the coupled-perturbed dual-basis self-consistent field equations (DBCPSCF) can now be solved within the space spanned by the small basis and additional computational savings can be obtained during the contraction of the separable two-particle density matrix with the set of AO integral derivatives. Both of these features lead to significant computational savings among molecules containing less than 100 atoms and extend the regime of molecular systems that can be optimized at the MP2 level of theory. Chemical accuracy and computational timings of the DB-RI-MP2 analytical gradient were demonstrated by optimizing a test set of 136 equilibrium molecular structures at the double- and triple- ζ levels and comparison to RI-MP2/aug-cc-pVTZ optimizations of several benzene dimer configurations. An application of the DB-RI-MP2 analytical gradient is also presented, in which several low-lying configurations of the benzene dimer are optimized using DB-RI-MP2 theory in an attempt to further characterize the its complex potential energy landscape.

Vibrational Corrections to Molecular Properties

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Molecules are never at rest. Even at 0 K molecules possess zero point vibrations giving rise to zero point vibrational corrections (ZPVC) to both energies and molecular properties. At higher temperatures the remaining set of molecular vibration levels begin to become populated according to the Boltzmann distribution giving rise to temperature averaging of energies and molecular properties. For molecular properties not just the electrons interact with e.g. an electric field, also the nuclei interact although the pure vibrational (PV) contribution is generally smaller than the pure electronic one which is routinely calculated using one of the well established electronic structure methods. These methods usually only calculate energies and molecular properties at the equilibrium geometry, completely neglecting the contributions from the dynamics of the molecule in question.

Vibrational wave functions (WF) are calculated within the Born-Oppenheimer approximation using the Midas program with potential energy surfaces, property surfaces, and normal modes calculated by the Dalton program at the density functional (DFT) - and coupled cluster (CC) levels of theory, including ZPVC to spin-spin coupling constants and ZPVC and PV corrections to non-linear optical properties. From the vibrational WFs, PV first hyper polarizabilities have been calculated using a new quadratic response approach recently implemented for explicit anharmonic vibrational configuration interaction WFs in the Midas program. The total (electronic and vibrational) frequency-dependent first hyperpolarizability has been calculated for a number of molecules for a range of optical frequencies as well as at the static limit.

Nonadiabatic Photodynamics of Aromatic and Heteroaromatic Rings*

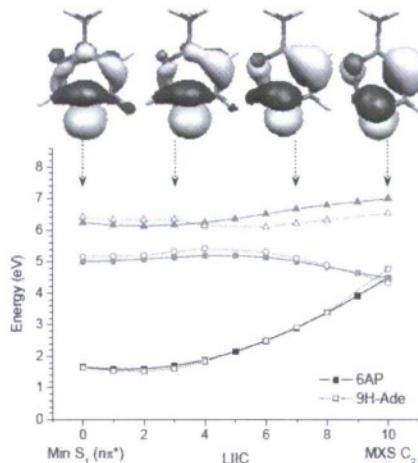
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Upon the photoexcitation, some aromatic and heteroaromatic rings can radiationless return to the ground state within few picoseconds, while others remain in the excited state for much more time until deactivate by photoemission. The difference between these two kinds of systems is the availability of conical intersections - degeneracy between the ground and the excited states - that allow the ultrafast conversion. Although it is normally possible to find conical intersections for any of these systems, they may be hidden by barriers or simply occur at too high energies to be accessible with the photon energy. In order to understand the general underlying phenomenon we have investigated several of such cases, namely the 6-membered rings aminopyrimidine, pyridone, and thymine and the 5-membered rings pyrrole, furan, imidazole, cyclopentadiene and thyophene. The research has been conducted by means of high-level *ab initio* calculations, with optimization of stationary points, search of conical intersections, and determination of reaction paths obtained at CASSCF and MRCI levels. Classical and surface-hopping direct dynamics have been performed using the program NEWTON-X [1] interfaced with the COLUMBUS [2] package, both developed in our group. In the examples discussed, we show how the structure of the out-of-plane conical intersections can be understood in terms of simple biradical models. How these same structures appear in different systems giving rise to classes of conical intersections. In which way (figure) and how long the molecule takes to reach the conical intersection. How the topography of the conical intersections influences the final products of the photoreaction.



References:

[1] NEWTON-X: www.univie.ac.at/newtonx
 [2] COLUMBUS: www.univie.ac.at/columbus

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[PI-66]

**Perturbation Expansion Based on Locally-Projected
Molecular Orbitals for Molecular Interaction**

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In studying molecular clusters having many molecular units with the ab initio MO methods, it is important to avoid the basis set superposition error (BSSE) as possible. The two-body counterpoise correction (CP) is widely used. But as pointed out by Valiron and Mayer (Chem. Phys. Lett. 275 (1997) 46), when the number of molecular units is larger than three, the many-body terms have to be taken into account; it requires repeated computations for monomers, dimers, trimers in the cluster with various sizes of basis sets. We have been developing the locally projected (LP) MO based perturbation expansion which is efficient and has less BSSE [1]. The method is applicable to large clusters with almost uniform errors, independent of the number of units. The locally projected MO is extended to the high-spin restricted SCF MO [2]. In the perturbation expansion, the proper choice of the excited orbitals is important to avoid not introducing the BSSE. When the excited orbitals are restricted to the strictly monomer basis set (SMBS) as the occupied SCF MOs in LPMO are, the “BSSE free” binding energy is obtained. It is demonstrated for the medium size of the basis sets that by adding some of the partially delocalized excited orbitals in the single excitation perturbation theory (SPT) the calculated binding energy becomes close to the counterpoise corrected Hartree–Fock binding energy and that if all of the excited orbitals are included, a part of the BSSE is recovered. The required cpu for the LPMO–SPT is less than for a supermolecule SCF calculation, in particular for larger clusters.

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[PI-67]

Degenerate Four-Wave Mixing in solution by Cubic Response:

The Polarizable Continuum Model

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We have derived and implemented the solvent contribution to the Cubic Response Function for the Polarizable Continuum Model in its Integral Equation Formulation. The present formulation is valid both at the Hartree–Fock and Kohn–Sham Density Functional levels of theory, since both bear the same formal description of the solvent contribution through an additional term in the Hamiltonian operator. This new implementation can be applied to large size systems (since a parallel formulation has been used) in order to calculate both static and frequency dependent third-order properties. We compute the solvent effect, both at the HF and DFT (B3LYP and CAM-B3LYP) levels, for the Degenerate Four-Wave Mixing (DFWM) process on three different classes of heteroaromatic chromophores: (I) triazine, benzoxazole, benzimidazole and benzothiazole; (II) three benzothiazole derivatives; (III) three tri-s-triazine derivatives. The results are discussed in terms of the solvent effects on the calculated property and compared to experimental data if available. The overall solvent effect has been found to be quite large and dependent on the considered substrate, but also on the chosen method: in general, the solvent effects are more pronounced at the DFT level than at the HF level. For the smallest molecules HF underestimates the experimental results, while DFT shows a good agreement. For Group (II) the HF results lead to better agreement with the experiments compared to the DFT counterparts, which, in most cases, are affected by resonance conditions.

[PI-68]

An IEF-PCM study of solvent effects on the Faraday B term of MCD

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Optical activity is in general a property of chiral systems. This property can however be induced in any system by the presence of an external magnetic field. One important manifestation of this phenomenon is the magnetic circular dichroism (MCD), in which one measures the differential absorption of left and right-circularly polarized light when a sample is subject to an external magnetic field. MCD can be rationalised in terms of three magnetic rotatory strengths, known as the Faraday A, B and C terms. Of these the Faraday B term is the only having non-zero contributions for a sample of molecules without degeneracies in the ground or excited states. We present the first theoretical investigation of solvent effects on the Faraday B term of MCD at the density-functional level of theory. In our model, the solvent is described by the polarizable continuum model in its integral-equation formulation. The B term is expressed as single residues of a quadratic response functions. We present the necessary extensions for including the effects of a dielectric continuum. The new code is applied to the study of the Faraday B term of MCD in a series of benzoquinones. It is demonstrated that electron correlation effects as described by density-functional theory is essential in order to recover the experimentally observed signs of the B term. Dielectric continuum effects increase in general the magnitude of the B term, leading to an overestimation of the experimental observations in most cases.

[PI-69]

High Level Ab Initio Studies on Enol-Keto Tautomerization Energetics

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A striking discovery in combustion research recently [C. A. Taatjes et al., *Science* 2005, 308, 1887.] was that two-, three-, and four-carbon enols are common intermediates of hydrocarbon oxidation in flames. It has been thought that enol concentrations are depleted via tautomerization to ketones; an endothermic process. However, this is a concept that has been challenged, based on activation energies for tautomerization emanating from early theoretical works. These theoretical values were obtained using methods ranging from semiempirical theory up to configuration interaction, limited to single and double excitations (CISD). We extend these studies by examining a range of reactive species using state-of-the-art methods, and present data for this oft-neglected enol-keto tautomerization process. Three enol-keto pairs that have been detected in combustion environments (vinyl alcohol/acetaldehyde, 2-propenol/acetone, and 1-propenol/1-propanal) are scrutinized. We have obtained geometries at the highly accurate CCSD(T)/cc-pVTZ level. Additionally, we use the focal point method to systematically extrapolate the energies to the complete basis set (CBS) limit, while accounting for electron correlation up to the coupled cluster with full single, double and triple excitations (CCSDT) level. Structures, reaction profiles, enol-keto energy differences, and activation barriers are presented, discussed, and compared to existing experimental measurements and earlier theoretical works.

**Structure and Intramolecular Interactions
in Peptide Nucleic Acids and in Some Derivatives***

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Peptide nucleic acids (**PNAs**) have a pseudopeptide backbone with **B** nucleobase side chains. They have high chemical and biological stabilities, and they are potential antisense and antigenic therapeutic agents. The effects of intramolecular interactions – either at the side chain or the backbone – upon the secondary structure of small oligomers of **PNAs** are not well known. In order to find the most important interactions, which have the highest effect on the structure, a theoretical study was initiated to support/predict the experimental results on **PNA** and new chiral nucleoside analogues termed azetidine nucleic acids (**ANA-1**).

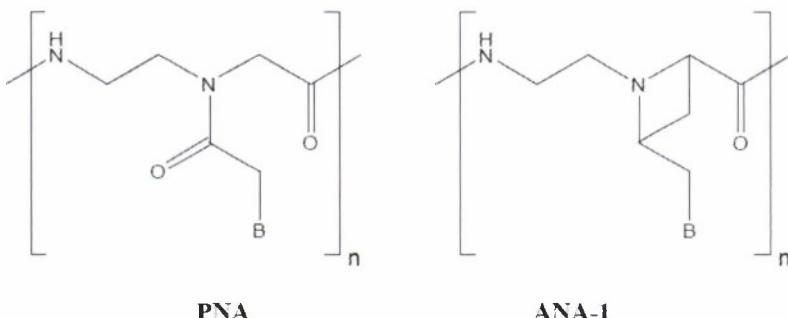


Fig. 1 The structure of **PNA** and **ANA-1** (**B**, nucleobase: A, U, C, G, T)

The possible structures of Ac-PNA-NHCH₃ and Ac-ANA-1-NHCH₃ models ($n = 1$) - in neutral and in protonated states - were first evaluated by a systematic conformational search using the PM3 semiempirical quantum chemical method implemented in Hyperchem. The best structures were then calculated by *ab initio* HF and DFT B3LYP (6-31G*, 6-31+G**) methods. The structural changes in small oligomers ($n = 6$) were calculated by 5-10 ns molecular dynamics calculations applying the GROMACS force field and the methods implemented in YASARA.

* Financial support from grant OTKA K61577 is gratefully acknowledged.

[PI-71]

Stability and SQM Vibrational Spectra of Carbo-nitrenes

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The stability of the carbo-nitrene biradicals and their isocianate isomers have been investigated by ROHF and RHF, as well as by RO-B3LYP and B3LYP methods. The carboalkyl- and carbosilyl nitrenes of triplet ground state are less stable than the corresponding isocianates of singlet ground state. The situation is just the opposite for the carboalkoxy- and carbosiloxy-nitrenes, according to the experimental observations [1]. The carboamino-nitrenes rearrange to isocianate structures. The ROHF/RHF results are qualitatively correct, but the RO-B3LYP/B3LYP calculations show a right tendency only. The IR spectra of the species were calculated in harmonic approximation at the RO-B3LYP/B3LYP levels. The theoretical force fields have been scaled by a single scale factor and using the Pulay-type SQM (selective) scaling method [2-4] as well. Recording of matrix isolated IR spectra of the compounds is planned.

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[PI-72]

**Anharmonic Vibrational Excitation Energies from
Vibrational Coupled Cluster Response Theory**

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Molecular vibrations are anharmonic by nature. To obtain accurate energies and properties of molecules this has to be taken explicitly into account when solving the vibrational Schrödinger equation. Vibrational coupled cluster (VCC) theory is based on an exponential parameterization of the wave function using the theory of second quantization. The VCC method typically gives higher accuracy than a corresponding vibrational configuration interaction (VCI) calculation with the same number of parameters. The VCC approach is ideally suited for application of response theory to obtain vibrational excitation energies as well as properties. This poster presents the underlying theory of VCC response theory as well as calculated excitation energies. The quality of different types of excitation energies, i.e. fundamentals, overtones and combinations are discussed theoretically and illustrated numerically.

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[PI-73]

Revealing Photochemical Mechanisms by *ab Initio* Quantum Dynamics: Case Study of Nitrophenols and Glycine

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In the *ab initio* molecular dynamics approach, the equations of motion for both electrons and nuclei are solved simultaneously as the simulation proceeds (direct dynamics). This approach is a hopeful tool for revealing reaction mechanisms: the dynamical equations are automatically leading us to important structures without any bias by our expectations. In many important cases the nuclear equations of motion have to include quantum effects. Specifically, quantum dynamics has to be employed for the description of non-adiabatic processes or when tunneling of light particles is involved. This is almost always the case of photochemistry. Full Multiple Spawning (FMS) method [1] is one route for this connection between quantum molecular dynamics and electronic structure calculations.

In this presentation we show usefulness of combining static electronic structure calculations with *ab initio* quantum molecular dynamics. Two examples are presented in detail: photochemistry of nitrophenols and photochemistry of glycine [2].

It has been recently shown that o-nitrophenol can potentially play an important role in photochemical production of HONO in the lower troposphere. The HONO structure is formed via hydrogen transfer from the OH group to the NO₂ moiety. We have studied the energetics of this process both in the excited state and the ground state showing possibility of this process. Furthermore we have calculated the timescale on which the hydrogen transfer occurs and also a duration of the non-radiative quenching to the ground state. Yields of different reaction products have been also calculated [3].

Study of glycine photochemistry has been motivated by a recent experimental and theoretical works on peptide photochemistry. We have addressed a question whether conformationally dependent photochemistry can be found in glycine. While static *ab initio* calculations left this possibility open, dynamical calculations have shown the opposite since one of the channels is entropically forbidden. Photochemical routes of glycine are discussed in detail.

Some methodological aspects of the dynamical calculations will also be presented [4].

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SECOND POSTER SESSION

**Topological Analysis of Conical Intersection Seams:
Characterization and Interconnection of Critical Points**

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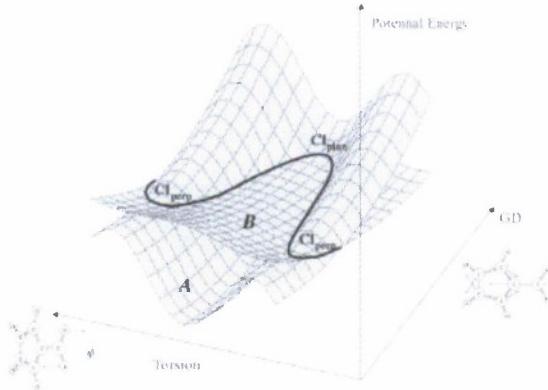
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Seams of conical intersection are analyzed in a way analogous to single Born–Oppenheimer (BO) potential energy surfaces. The analysis comprises the following two aspects: (1) Characterization of optimized conical intersection (CI) points on the basis of the Hessians of the degenerate states. The characterization is based on a set of curvilinear coordinates which preserve the degeneracy to second-order and define the seam of CI. The second derivatives of the energy along these coordinates give the curvature of the CI seam and are used to characterize the critical points as local minima or saddle points in the (N-2)-dimensional space of intersection, in analogy to minima and transition structures on a BO potential energy surface. (2) Interconnection of critical points with minimum energy path and relaxed scan optimizations in the intersection space.



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Adiabatic Jacobi Corrections for H_2^+ -Like Systems

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Chemical thinking has been based principally on the Born–Oppenheimer (BO) approximation, which separates the motion of electrons from that of nuclei. Nevertheless, the BO scheme is just an approximation, based on the notion of infinite nuclear masses. Traditionally, a first-order perturbative energy correction, the so-called diagonal BO correction (DBOC) has been advocated and used to move simply beyond the BO approximation. We have developed a variational technique that provides a new way to perform non-BO computations [1]. Our adiabatic method, which applies fixed internuclear separations in a Jacobi coordinate system, allows the use of proper, finite masses for the nuclei while maintaining the notion of potential energy curves. The new method is able to characterize the unique energetics of the different isotopologues of a molecule. The newly defined adiabatic Jacobi corrections (AJC), which correspond to the energy difference between energies from finite and infinite nuclear mass computations, have been computed for H_2^+ , D_2^+ , and HD^+ at fixed internuclear separations. It is shown that the AJCs differ from the traditional DBOCs and have a more clear meaning when the molecule dissociates. Unlike the BO scheme, our technique does allow for asymmetry in HD^+ , for example, and allows its proper dissociation to D and H^+ . Expectation values of the proton-electron and deuteron-electron distances for HD^+ have been computed and compared to the results of the fully nonadiabatic approach. Exact and approximate analytical and numerical results are given for counterfactual systems as well.

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**State-of-the-art Semiempirical MO Calculations:
Case Studies in Modelling Metallopeptides**

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The recently introduced PM6 method by J. J. P. Stewart is utilized for MO calculations on structural motifs in metal-binding peptide sites. The compounds investigated include molecules of major physiological and pharmaceutical importance, such as the Alzheimer's disease amyloid beta-peptide fragments and superoxide-dismutase mimetics. PM6, implemented in the MOPAC2007 package[1], is a new and more accurate NDDO parameterization representing a major improvement over the traditional AM1 and PM3 methods. Heats of formation data can be calculated more accurately, and weaknesses of the earlier semiempirical MO methods in treating hydrogen bonds and amide linkages are corrected. All transition metals can be handled as well. The performance of PM6 is illustrated by the case studies presented here: full optimization of copper(II), copper(I), zinc and nickel complex structures involving up to 16 amino acid residues (over 250 atoms) were routinely carried out on commodity PCs. The MO calculations offer new insight into the structure and activity of these important biomolecules.

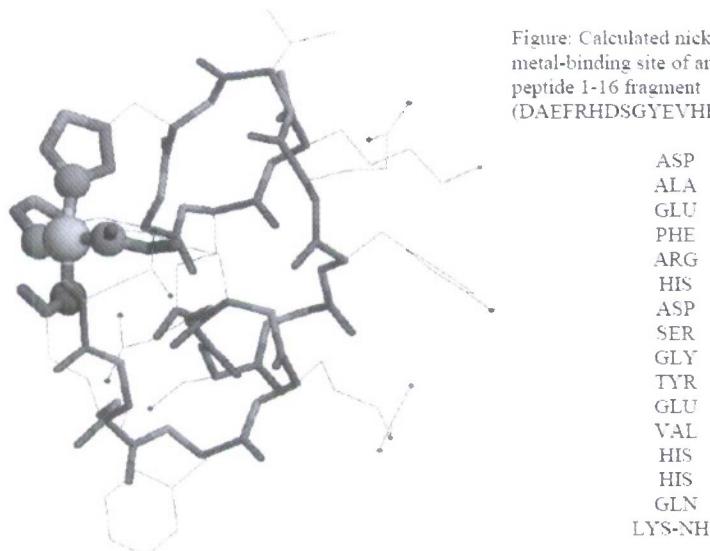


Figure: Calculated nickel-complexed metal-binding site of amyloid *beta*-peptide 1-16 fragment (DAEFRHDSGYEVHHQK-NH₂).

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Photodissociation dynamics of trimethyltin iodideN. Ben Amor,^b D. Ambrosek,^a C. Daniel,^a R. Marquardt^a^a *Laboratoire de Physique Quantique UMR 5626 CNRS/ Université Paul Sabatier
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Organotin compounds have numerous applications as precursors of polyvinyl chloride stabilizers, biocides and antifouling agents in agriculture and industry. They have been used in the preparation of optically pure tin derivatives for asymmetric heterogeneous catalysis and they provide a means to change the refractive index and the structure of glass and glass gels [1]. Photochemical experiments reported on $(\text{CH}_3)_3\text{SnI}$ in various media indicate homolytic cleavage of the Sn-I bond following 254 nm irradiation leading finally to $((\text{CH}_3)_3\text{Sn})_2$ and I_2 . Both products would desorb from the glass during subsequent heating, precluding their involvement in gradient index formation [2].

In order to propose new laser control experiments, photodissociation dynamics of $(\text{CH}_3)_3\text{SnI}$ has been investigated in the semi-classical approximation and in the quasi-resonant approximation, as well as by direct numerical integration of the time-dependent Schrödinger equation with a one-dimensional model describing the Sn-I bond elongation. The simulations are based on potential energy functions (PEF) and associated dipole moments functions (DMF) obtained from non-linear fits of the MS-CASPT2 (Multi-State Complete Active Space 2nd Order Perturbation Theory) potential energies and dipole transition moments including spin-orbit effects [3,4]. Simulation of the excited states dynamics suggest that the ionic channel should be populated by irradiation at about 207 nm. The quantum yield of ionic products $((\text{CH}_3)_3\text{Sn}^+ + \text{I}^-)$ could be higher than 50 %, while the radical products $((\text{CH}_3)_3\text{Sn} \cdot + \cdot \text{I})$ should not exceed 10 % for pulse lengths of the order of 150 -200 fs in the 50 TW cm^{-2} range.

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A Restricted Quantum Reaction Path Hamiltonian for Large Polyatomic SystemsJavier González,^b Xavier Giménez,^a Josep Maria Bofill^b^aDepartament de Química Física i Centre especial de Recerca en Química Teorica,
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A derivation of a Quantum Reaction Path Hamiltonian (Q-RPH) is proposed, which is based on a formulation of the classical version by González, Giménez and Bofill [J. Phys. Chem. A **105**, 5022 (2001)]. The method is based on a coordinate mapping, from the general $3N-6$ dimensional space, to the mathematical one-dimensional space of a reference curve embedded in the complete problem. The effects of curvature, i.e. of mode coupling, appear as a position-dependent mass term within the mapped one-dimensional space. It is thus a quantum dynamical problem with variable inertia, the latter depending on the perpendicular gradients and the vibrational frequencies.

The formulae are derived for any kind of reaction path, even though it is presently focused on the Intrinsic Reaction Coordinate path (IRC). The combination of this Quantum RPH, with a Discrete Variable Representation method (DVR) for the time-dependent wavepacket propagation, results in an algorithm suitable for the calculation of real-time quantum dynamics of chemical reactions involving polyatomic molecules. Eckart, Muller-Brown and $\text{H} + \text{H}_2$ potentials have been studied as test cases.

[PII-6]

Perfluorinated Polycyclic Aromatic Hydrocarbons: Benzene, Naphthalene, Anthracene, Phenanthrene, Pyrene, Tetracene, Chrysene, and Triphenylene

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Although benzene and naphthalene do not have electron affinities in the conventional sense, perfluorobenzene and perfluoronaphthalene have nonzero electron affinities. Theoretical methods extensively calibrated with experiment for the prediction of electron affinities (EAs) predict the EAs of perfluorobenzene, perfluoronaphthalene, perfluoroanthracene, and perfluotetracene as 0.69, 1.02, 1.84, and 2.39 eV, respectively. Thus are predicted to be effective electron acceptors. The electron affinities depend not only on the size of the perfluoro polycyclic aromatic hydrocarbons (PAHs) but also on the structural arrangement. For $C_{14}F_{10}$, the electron affinities for perfluoroanthracene and perfluorophenanthrene are 1.84 and 1.41 eV, respectively. For $C_{18}F_{12}$, the electron affinities for perfluorotetracene, perfluorochrysene, and perfluorotriphenylene are 2.39, 1.83 (C_1) or 1.88 (C_2), and 1.76 eV, respectively. The influence of the structural arrangement is more pronounced than the size effect. Thus, it should be possible to combine these two effects to achieve the design of the perfluorinated PAH molecules with the electron affinities in pre-described ranges.

[PII-7]

Theoretical Prospects towards Understanding the Chirality of Fluoxetine in Drug-Ligand Interaction

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Fluoxetine exists in racemic mixture and the importance of S and R form as an antidepressant with regards to the chirality has been taken into consideration in this report, so as to investigate different type of interactions, associated with the neurotransmitter, serotonin¹ using different quantum chemical methods. The electronic structure calculations for serotonin monomer, fluoxetine monomers and the six stable conformations of the serotonin – fluoxetine complexes have been performed at ab initio and density functional theory (DFT) methods (HF/6-31G**, HF/6-31+G* and B3LYP/6-31+G*). Harmonic vibrational frequencies of serotonin monomer and fluoxetine monomers have been calculated at B3LYP/cc-pVTZ method. The results obtained for the serotonin monomer have also been compared to van Mourik and Emson's results.² Single point energy calculations at B3LYP/cc-pVTZ and B3LYP/aug-cc-pVTZ levels on HF/6-31G** and HF/6-31+G* optimized geometries have also been carried out, respectively to better estimate the hydrogen bonding strengths. However, the calculated hydrogen bonding energies are also corrected for the basis set superposition error (BSSE) at B3LYP/6-31+G* method. This work is to provide predictions and to help experimental and theoretical studies towards understanding the chirality of fluoxetine in drug-ligand interaction, associated with serotonin.

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[PII-8]

Projector Monte Carlo Method Using Configuration State Functions

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To use massively parallel computers, theory and algorithm of high parallel efficiency are required. Diffusion (Projector) Monte Carlo method is a good candidate, however, the results depend on the trial functions when we employ the fixed-node approximation that is widely used. In this study, we use configuration state functions (CSFs) instead of particles in Projector Monte Carlo method to avoid the dependence of results on the trial functions. The main differences from the conventional DMC calculations are as follows: (i) The propagator is approximated as $\exp(-\Delta\tau \hat{H}) \approx 1 - \Delta\tau \hat{H}$, (ii) CSFs are sampled with their signs. In test calculations on small molecules, the results were in good agreement with the Full-CI ones. In the poster session, we will discuss the dependence on the number of CSFs, time step dependence, and the validity of the approximation: $\exp(-\Delta\tau \hat{H}) \approx 1 - \Delta\tau \hat{H}$.

[PII-9]

Spin-Component Scaling in Intermolecular Interactions

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Non-covalent interactions involving nucleic acid base pairs are important driving forces for processes such as the folding of nucleic acids, molecular recognition and the activity of anti-cancer agents. Hydrogen bonding between nucleic acid base pairs can be easily and accurately treated with computationally inexpensive techniques such as HF and DFT along with relatively modest basis sets. However, the stacking interactions in such situations are dominated by London dispersion forces which are much less computationally tractable and typically only accurately described by coupled cluster theory with large basis sets.

By combining the spin-component scaled (SCS) variant¹ of MP2 with density fitting and local correlation treatments, it is shown that it is possible to reproduce CCSD(T)/aug-cc-pVQZ binding energies for all three major conformations of the benzene dimer along potential energy scans of monomer separation with a substantially reduced computational cost.

Although the benzene dimer is often regarded as a prototypical example of π - π stacking, upon applying this same methodology to a series of ten stacked nucleic acid base pairs it is apparent that the default SCS scaling parameters provided, on average, less accurate interaction energies than unscaled MP2. Hence, a new set of scaling parameters are obtained by minimising the rms error in interaction energies over all ten stacked nucleic acid base pairs when compared to the best available literature values. These new parameters, termed spin-component scaled for nucleobases (SCSN), were then validated against a training set of non-covalent interactions known as S22² and provide results in excellent agreement with the best estimates.

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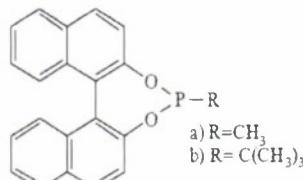
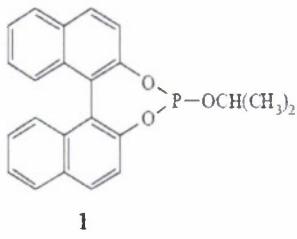
**Theoretical Study of Rhodium-Catalyzed Assymetric
Hydrogenation with Monodentate Phosphorous Ligands**

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The Rh-catalyzed asymmetric hydrogenation of olefins using monodentate phosphites as ligands is becoming increasingly popular compared to the use of traditional chelating bidentate ligands. The catalytic mechanism involving such bidentate ligands has been studied in detail, whereas very little is known about how Rh-catalysts with monodentate ligands react. Mechanistic studies on Rh-catalysts with monodentate phosphite ligands **1** (see figure) showed that the dominant product is formed from the more stable intermediate substrate/catalyst adduct [1]. This is in contrast to the results for the bidentate ligand catalysts studied by Halpern for a similar reaction [2]. Further experimental reports using monodentate phosphonite ligands **2** (see figure) showed a large variation of the enantiomeric excess.



The catalytic mechanism involving complexes containing **1** as ligands is studied using DFT [3] and is compared with the previously proposed mechanism involving bidentate ligands. Our calculations show that the rate determining step for the chelating ligand model is the insertion of hydrogen into the catalyst/substrate adduct. In the monodentate model, the rate determining step appears later in the catalytic cycle. The major product of this reaction is determined by the relative stability of the catalyst/substrate adduct complex. Furthermore, we have studied several combinations of the substrate/adduct complexes of type RhLL (where L=(R)-2 or (S)-2) to verify the mechanistic model, and the results are compared to experiment data.

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[PII-11]

Excited States in Solids

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There are two very different approaches to electronic structure calculations of transition metal oxides. On the one hand, an embedded cluster ansatz can be used to investigate local phenomena such as adsorption processes, d-d excitations of transition metal centers, magnetic exchange coupling, defects, and so on. We will show results of embedded cluster calculations for ground and excited states of magnetic impurities [1] and oxygen vacancies [2] in ZnO. On the other hand, it is of great interest to consider the periodic boundary conditions of a crystal explicitly. For this purpose, a valence CI method based on a periodic Hartree-Fock calculation will be presented. In the framework of this method it is possible to include the coupling of excitations at different transition metal centers. We investigate the influence of this coupling for d-d excitations in transition metal oxides and compare the results of our approach to embedded cluster calculations [3] and super cell calculations [4].

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[PII-12]

Benchmark Studies of Projection and Variational Coupled Cluster Theories

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In traditional coupled cluster theory (TCC), equations for the amplitudes are obtained by projecting Schrödinger's equation onto the manifold of excited determinants. This approach has the advantage of simplicity: the equations terminate at finite order in the cluster operator. However, the resulting energy is not a variational upper bound. Truly variational approaches (for example, variational (VCC), extended (ECC), unitary (UCC)) have been proposed previously,¹⁻³ but have not been widely used because they are more difficult to implement, and TCC is found numerically to work well.

In this work, we explore numerically the relative performance of TCC, VCC, UCC and ECC with a view to using them, or approximations to them, in situations where correlation is strong, for example in dissociating molecules. The methods are implemented in a general way within a full CI code, with up to quadruple excitation operators, and using both spin-restricted and unrestricted reference wave functions.

It is found that where correlation is predominantly dynamic all of the approaches give essentially the same result, but for dissociating molecules, VCC and ECC are far superior to TCC.

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[PII-13]

The Use of Genetic Algorithm in Simulating and Fitting ENDOR Spectra From Structural Parameters

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ENDOR spectroscopy is a powerful tool for determining hyperfine interactions between spin active nuclei and unpaired electrons in transition metal complexes. In many such systems, the powder ENDOR pattern arising from the protons of the ligands is dominated by the anisotropic dipole-dipole contribution to the hyperfine coupling, and its accurate extraction and subsequent analysis using a point dipole model can be used to determine structural coordinates of the protons. Previous studies from our group have used this approach to successfully model the structure of the protons in a series of oxovanadium vanadyl salen complexes in various solvents, with good agreement with DFT optimised structures. A requirement of the accurate determination of the complete hyperfine tensor is the simultaneous computer simulation of the ENDOR spectra recorded at the turning points of the EPR spectrum. This study aims to further develop the complementarity between ENDOR simulations and DFT by developing code to automate the process of linking the structure and the spectra. DFT optimisations are used to generate a set of initial coordinates (as well as isotropic hyperfine coupling contributions), which are then used to generate the associated A-tensors. The spectrum is simulated, and compared to the experimental spectrum, with this comparison being the fitness criterion in a genetic algorithm optimisation of the structural coordinates. The ENDOR spectrum, in the context of the point dipole model, is thus used as a refinement to the DFT structural data. This process has been tested using the simple axial spectra of the $\text{VO}(\text{acac})_2$ complex.

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[PII-14]

Higher-Order SCF Response

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Combining quasienergy [1] and Lagrangian formalisms, we derive and compute response functions as derivatives of the SCF quasienergy Lagrangian with respect to external perturbations (static or dynamic). In the Lagrangian formalism, application of the $2n + 1$ rule is straightforward. Our code handles linear and nonlinear (geometry, GIAO-magnetic) perturbations, to any order, given that the corresponding integrals have been implemented. By using the AO density matrix as basic parameter, we avoid the issue of „orbital connection”. Examples are presented.

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[PII-15]

MP2 in the Projected Atomic Orbital Basis

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Methods to calculate correlation energy contributions using the second order Moller-Plesset (MP2) perturbation theory and coupled-cluster (CC) theory in large molecular systems are mostly based on the idea of localized orbitals [1,2]. In those approaches, the low-power scaling is then obtained by dividing the molecule into domains and applying a some form of distance screening. Although the most of the problems related to the domain division can be circumvented in practice, the distance dependence is still there, which cancels the important black-box nature of CC methods. Local correlation approaches has been presented in the atomic orbital (AO) basis as well [3], but they feature poor convergence characteristics because of the non-diagonal-dominant Fock matrix.

Our approach is based on the projection of atomic orbitals to occupied and virtual spaces leading to the over-complete projected atomic orbital (PAO) basis [4,5]. In which the AO-basis is orthogonalized before the projection. Our formulation leads naturally to a local correlation approach without ad-hoc parameters and with good convergence characteristics even in systems with very delocal electronic structure.

Here, we will present an implementation of PAO-MP2 and discuss issues related to different orthogonalization schemes, convergence and sparsity. Initial CPU-timings of the implementation are also presented.

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Computational Study of the Hydrogenolysis of Hydroxymatairesinol to Matairesinol

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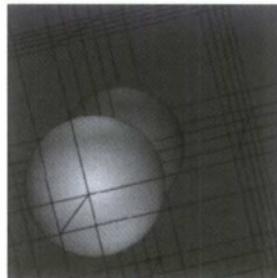
The title reaction, involving an interesting natural substance already proposed as a chemopreventive agent against cancers, has been recently studied on supported palladium catalysts [1-3]. There are two diastereomers of hydroxymatairesinol. To propose possible reaction mechanisms, an extensive conformational search on the two diastereoisomer reactants and on the reaction product has been performed, by allowing discrete rotations of significant dihedral bond angles. This allowed us to scan about 93 000 conformers per species. The conformers submitted to calculations (ca. 3000 per species) have been selected on the basis of distance and connectivity matrix check. The geometry of the select species was fully optimized at AM1 level whereas their energy was evaluated at HF/6-31G(D) level by single point calculations. This procedure let us to select about 20 conformers for each of the three species investigated. The geometry of the most stable conformers, and of a few high energy species, was further refined by optimization at B3LYP/6-31G(D,P) level, and the solvent effect evaluated by polarizable continuum methods. The reaction kinetics has been followed by considering the most stable reactants and products, and the role of the metal catalyst simulated by H_nPd_2 clusters ($n = 2,4$).

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Multiwavelet Tools for Quantum Chemistry: Recent Developments and AlgorithmsLuca Frediani,^a Tor Fla,^a Kenneth Ruud,^a and Eirik Fossgaard^b^a *Center for Theoretical and Computational Chemistry**University of Tromsø, N-9037 Tromsø, Norway*^b *International Research Institute of Stavanger, Thormohagensgate 55, 5008, Bergen*

In recent years, discretization techniques applied to Quantum Chemistry [1] have received renewed attention due to several factors: development in the underlying mathematical tools, design of new and efficient algorithms but also difficulties connected to the use of large atom-centered Gaussian basis sets especially for big systems. One such method is based on Multiresolution Analysis[2] and Multiwavelets[3] and has several attractive features like e.g bandedness of the involved operators and rigorous "a priori" error control. The former leads ultimately to linear-scaling algorithms whereas the latter allows to obtain results within a predefined accuracy from the complete-basis-set limit [4,5]. We here present our work towards the development and implementation of a Multiwavelet code for Quantum Chemistry calculations[6]. In particular we have developed and implemented a formalism for the application of separable integral operators in $d > 1$ dimensions using the Non-Standard (NS) form of operators. The proposed formalism is general, compact and oriented towards the practical implementation into a working code using multiwavelets. For the case of Poisson and Helmholtz operators which are the ones needed in connection with the integral formulation of the Kohn-Sham equations, we also propose a simple scheme for the generation of an approximate separated representation of the corresponding kernels with finite arbitrary precision. Such a representation, combined with the NS-form allows to build a sparse, banded representation of the operators. We have implemented a code for the application of the Poisson and Helmholtz operators on a separated Non-Standard form to a multivariate function. The implemented code computes explicitly all the 2^{2d} components of the d -dimensional operator in the NS-form. We finally demonstrate the performance of our implementation on some test cases.

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[PII-18]

Digging for Boron: DFT-based Genetic Algorithm Search for Energy Minima of B_{12} - B_{30}

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In a similar manner to a previous investigation of gold clusters [1], gas phase ion mobility measurements were conducted on a series of B_n^+ clusters (n from 12 to 30). Several particular boron clusters in this range have been previously examined through theory [2-4], but to get reliable matches to the experimentally determined collision cross sections, we must undertake a systematic and extensive search for energy minima in the B_n potential energy space. A plethora of structure optimizations were conducted according to a hybrid *ab initio* genetic algorithm [5] using a small SVP basis and the BP-86 functional. The final populations of low energy structures and their cations were then re-optimized with the larger def2-TZVPP basis (11,6,2,1)/[5,3,2,1] and the TPSS functional. The program system TURBOMOLE was used throughout.

At this stage, the computed lowest energy structures fit well with experimental data. Clusters of boron show an unusually rich zoo of low energy structures, often with 10 isomers within an eV of the minimum. A notable exception being B_{20}^+ , an S_4 -symmetry cylinder (derived from the D_{10d} -symmetry neutral B_{20}) where the minimum energy isomer is over 1 eV more stable than any other structure. The dominant motif is of B_3 triangles tessellated into cylinders, planes (be they flat, curved, or puckered), and incomplete hollow spheres. There is a remarkable absence of space filling structures, quite different from Al or Ga clusters.

In addition to details of the algorithm's execution, this poster will describe practical aspects of its application to gas phase cluster characterization. For the smaller compounds, the algorithm quickly converges to a low energy population of structures that includes previously reported structures. As cluster sizes grow, the time to population convergence lengthens exponentially and extra-algorithmic measures (such as seeding with derivatives of the best structures of smaller clusters) must be taken.

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[PII-19]

QM/MM and Quantum Chemical Studies of Rhodopsin Chromophore

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Rhodopsin is a photoreceptor that mediates light/dark vision in the eyes of vertebrates. The chromophore of rhodopsin is 11-cis-retinal bound via a protonated Schiff base (pSb) linkage to Lys296. The counterion for the pSb is provided by Glu113 and is salt-bridged to the pSb. A water molecule (Wat2b) appears in the vicinity of Glu113 as part of the complex counterion. The trigger of the visual cascade is the photochemical cis-trans isomerization of the chromophore. The first intermediate is bathorhodopsin which contains a highly-twisted all-trans-retinal. Subsequent conformational changes eventually lead to the activation of the G-protein [1]. The first crystal structure of bovine rhodopsin was presented in 2000 and afterward the resolution was extended to 2.2 Å [2]. In 2006 the bathorhodopsin was crystallized and resolved at 2.6 Å resolution [3]. Based on the crystal structures [2,3] we investigate the chromophore geometries in rhodopsin and bathorhodopsin using a combined quantum mechanical / molecular mechanical (QM/MM) method [2,4]. For the calculations of the optical properties we employed the CASPT2 method to the chromophore with the complex counterion [5]. Rhodopsin (11-cis-retinal, $\lambda_{\text{max}} = 498\text{nm}$): The electron density map reveals the chromophore has a 6-s-cis, 11-cis-12-trans, 15-anti configuration, as predicted by NMR experiments. QM/MM modeling work shows that different geometries found in the crystal structures converge to nearly identical geometry, where the central isomerizing bond (C11=C12) has a pre-twist with a negative helicity [2,4]. Bathorhodopsin (all-trans-retinal, $\lambda_{\text{max}} = 543\text{nm}$): The bathorhodopsin crystal structure reveals that the chromophore has characteristic torsion around the double bonds [3]. Modeling work shows that this chromophore geometry is stable inside the binding pocket. The calculated shift for rhodopsin model to bathorhodopsin model (36 nm) is in good agreement with that determined experimentally [5].

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[PII-20]

Calculation of vibrationally averaged g Tensors at the Coupled-Cluster level

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We present a new method for calculating the electrostatic potential directly in a straight forward manner. While traditional methods for calculating the electrostatic potential usually involve solving the Poisson equation iteratively, we obtain the electrostatic interaction potential by performing direct numerical integration of the Coulomb law expression using finite-element functions defined on a grid. The singularity of the Coulomb operator is circumvented by an integral transformation and the resulting auxiliary integral is obtained using Gauss quadrature. The three-dimensional finite-element basis is constructed as a tensor (outer) product of one-dimensional functions yielding a partial factorization of the expressions. The resulting algorithm has without using any prescreening or other computational tricks a formal computational scaling of $N^{(4/3)}$, where N is the size of the grid. We show here how to implement the method for efficiently running on parallel computers. The matrix multiplications of the innermost loops are completely independent yielding a parallel algorithm with the computational costs scaling practically linearly with the number of processors.

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[PII-21]

CC3 vs. CASPT2: A Comparison of Excitation Energies

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The vertical excitation energies for a diverse set of eighteen theoretically well defined organic molecules have been calculated using CC3. This data set is benchmarked against multiconfigurational second-order perturbation theory, CASPT2, which usually gives a proper description of the major features in electronic spectra. The calculations were performed at the same ground state equilibrium geometries (optimized with MP2/6-31G*) and the same basis set (TZVP).

The data set is chosen to cover some of the most important classes of chromophores, i.e. polyenes, amides, aromates and nucleobases. We found that, with some exceptions, the CC3 valence excited states come close to the reference CASPT2 values. A statistical evaluation of excitation energies and one-electron properties will be presented and the cases where significant deviations between these methods occur will be discussed.

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Towards Accurate Thermochemistry of Combustion Intermediates with ab Initio Methods: The Reaction of Ethyl Radical and O₂Jeremiah Wilke and Henry F. Schaefer*Center for Computational Chemistry, University of Georgia, Athens, GA 30602-2525, U.S.A.*

The reaction of ethyl radical with ground state O₂ is an important model reaction for hydrocarbon combustion. Much work has focused on ethylene formation because the reaction rate actually decreases in the range 600-1000 K. Theoretical work has supported a mechanism involving the concerted dissociation of ethylperoxy radical into ethylene and HO₂. The computed transition state is lower in energy than the initial ethyl and O₂ reactants, producing an overall negative barrier consistent with the experimentally observed kinetics. Kinetic modeling and empirically-corrected model chemistries predict this barrier to be approximately -3.0 kcal/mol. In contrast, the best *ab initio* data places the barrier higher than -1.0 kcal/mol. Since the exact barrier is necessary for accurate kinetic predictions, the energies of the ethyl-O₂ model system remain an important question. The focal point analysis of Allen et al. has been shown to predict thermodynamic properties that agree with experiment to kJ/mol accuracy. Using the focal point extrapolation scheme, we report *ab initio* computations of unprecedented accuracy on the ethyl-O₂ system to help resolve the theoretical discrepancies.

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**Electronic Structure, Dipole and Transition Dipole Moments
of HCl^+ and HBr^+ to Simulate the Dissociation Dynamics**

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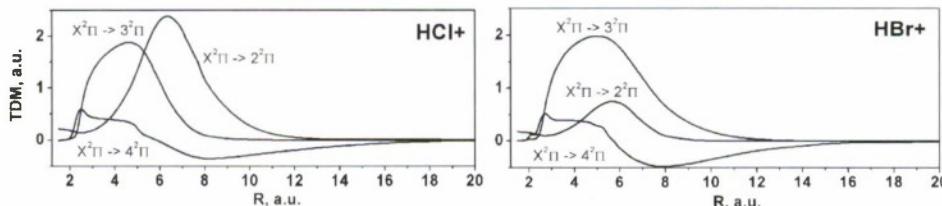
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Photofragmentation of diatomic hydrogen halides is a prototypical photochemical reaction, it serves as good model of fundamental molecular physics and also for the state-of-the-art of ultrafast laser chemistry. In order to investigate the prospect of controlling the photo fragmentation of HCl^+ and HBr^+ ions and understand the mechanism of this process with many excited states we undertook a joint theoretical and experimental research using in theory ab initio approaches to electronic structure calculation and in experiment the pump-and-probe femtosecond spectroscopy. The photofragmentation process is simulated by: (i) *ab initio* calculation of a series of electronic states of these ions with the symmetry adapted cluster – configuration interaction (SAC-CI) method; (ii) evaluation of dipole moments and transition dipole moments (TDM) from the *ab initio* wave functions [1]; (iii) numerical solution of coupled time-dependent Schrödinger equations for a series of the optically important states [2]. The figure below displays the data derived for selected TDM from the ground state ($\text{X}^2\Pi$). Remarkably, the main maxima for this series of transitions appear at the different separations of atoms, that provides possibility to control the photofragmentation by tuning parameters of laser pulses used for the excitation.



Time-dependent calculations of the photofragmentation dynamics confirm this possibility and show the importance of different kind of coherent effects on the yield for different reaction channels [2]. These yields are controlled by photon energy, radiation power, chirp parameter, and carrier envelope phase of laser pulses used. Complementary experimental study [3] and its interpretation in the light of recent calculations are discussed.

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[PII-24]

**Global ab Initio Potential Energy Surface and Dynamics
of the $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$ Reaction**

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The reaction of the H atom with silane, $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$, is an important step in the mechanism of thermal decomposition of monosilane, and plays a significant role in the chemical vapor deposition processes used in the semiconductor industry. As a prototype of exothermic polyatomic hydrogen abstraction reactions, it has been investigated by many experimentalists and theoreticians over the decades [1-6]. The full-dimensional ab initio potential energy surface (PES) for the title reaction is a 12-dimensional hypersurface, the construction of which still remains a serious challenge. The dynamics on the accurate PES of reaction system can provide important information for the studied system. The present work focuses on both the construction of global ab initio PES and dynamical calculations for the title reaction. The first global ab initio 12-dimensional PES for the $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$ reaction, referred to as the WSB surface, was constructed using the modified Shepard interpolation method proposed by Collins and co-workers [7-9]. This PES[10] is based on extensive calculations for the energy, the first and second energy derivatives at the UQCISD/cc-pVTZ level of ab initio theory. Using the WSB surface, the classical trajectory calculations were performed to demonstrate the convergence of the PES with respect to the size of the data set and to study product energy distributions. Variational transition state theory calculations were also carried out on WSB, yielding rate coefficients in general good agreement with the available experimental results. Detailed quasiclassical trajectory (QCT) [11] studies have been carried out for the $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$ reaction using WSB PES. The QCT excitation function, product rovibrational populations, internal energy distributions, and the thermal rate coefficients were investigated in detail and compared with some related data.

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[P11-25]

Normal Modes in Partially Optimized Molecular Systems

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In molecular modeling extended systems are often only partially optimized in order to restrict the computational cost. For instance in a first step the whole system is optimized at a low level-of-theory, and in the next step only part of the atoms, usually the chemically active part of the molecule, is optimized at a high level-of-theory, while atoms in the passive part are kept fixed at their original positions. Another example of partial optimization is the simulation of defects embedded in a lattice. It is common practice to model a crystal by cutting out a cluster and keeping the cluster border atoms fixed during the geometry optimization, to prevent unphysical deformations of the cluster (falling apart or collapsing).

Partially optimized geometries are non-equilibrium structures. To calculate normal modes the usual NMA (normal modes analysis) equations could be solved, but this procedure shows some serious defects. The second derivative matrix of the potential energy (Hessian) with respect to all the Cartesian coordinates has only 3 zero-eigenvalues instead of 6, implying that the rotational invariance of the potential energy surface is not manifest anymore. Spurious imaginary frequencies appear. Moreover the eigenvalues of the second derivative matrix depend on the choice of coordinates.

In the Partial Hessian Vibrational Analysis (PHVA)^{1,2} these defects are surmounted by giving the fixed part an infinite mass. We propose the Mobile Block Hessian (MBH) model³ as an improvement of the PHVA. In the MBH model the fixed part is considered as a rigid block that is allowed to participate in the small amplitude vibrations, thus taking into account the finite mass of the fixed block. The spurious frequencies and the coordinate dependence are avoided since the system of optimized atoms plus block is in equilibrium. As the method only requires a sub matrix of the Hessian, a reduction in computer time can be obtained. The MBH was generalized to the case of several mobile blocks.

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**Generalization of Equation of Motion Coupled Cluster Method to a State Selective
Internally Contracted Multireference Coupled Cluster Approach**

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The Equation of Motion Coupled Cluster Method (EOMCC) has seen a large number of successful applications to excited states. This method is applicable primarily to singly excited states that have a ground state (or more generally a parent state) that is well described at the single reference level.

In this poster we discuss the generalization of EOMCC to systems that require a multiconfigurational description of the parent state. The parameterization of the wave function is reminiscent of EOMCC and employs a spin-adapted cluster operator, \hat{T} , that excites from occupied and active orbitals into the virtual space. The transformed Hamiltonian $e^{-\hat{T}} \hat{H} e^{\hat{T}}$ is subsequently diagonalized over an active space plus single excitations. Key features of the method are: (i) The approach can be used to target a specific state or a small number of states in a state-averaged fashion. The cluster amplitudes are optimized precisely for the states of interest. (ii) The occupied and active orbitals are defined in a Brueckner like fashion: the reference state is determined in the presence of dynamical correlation effects. (iii) The approach is classified as an internally contracted multireference CC approach and is fully spin-adapted. (iv) The most expensive part of the calculation is the diagonalization of a transformed Hamiltonian, which contains three-body interactions over an active space plus single excitations. This is accomplished by an efficient direct CI approach and a factorization of the three-body terms. (v) Further extensions of the approach akin to the similarity transformed EOMCC are possible, see the poster by Liguong Kong from our group.

[PII-27]

Orbital Optimization Using the Monotonically Convergent Density Matrix Renormalization Group Method

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Despite the success of modern quantum chemistry in addressing organic molecules the treatment of many inorganic systems revealing many close laying states is still not within quantitative reach for current methods. In order to treat the non-dynamical correlation we take advantage of the density matrix renormalization group (DMRG) method which became a very successful method in the field of solid state physics. Our prime goal is to develop a DMRG-SCF approach, analogous to CASSCF, but dealing with large active spaces, which are too demanding for FCI. As a first step towards the DMRG-SCF procedure we present a spin-adapted DMRG algorithm designed to target spin- and spatial-symmetry states which are hard to obtain while using an unrestricted algorithm. We show that the spin-adapted energies can be lower than the unrestricted ones, which is intuitively surprising based on the analogy with restricted vs. unrestricted Hartree-Fock approach. Our next step is modification of the DMRG algorithm in order to make the obtained energy lower at every step during sweep. The monotonically convergent DMRG (MC-DMRG) scheme lets us obtain a two-body density matrix as a byproduct of the existing procedure without any additional cost in storage. Additionally, a two-body density matrix produced at convergence using this scheme is free from N-representability problem which is present when producing the 2-body density matrix with two-site DMRG scheme without additional storage cost. Finally, taking advantage of the developed modifications we present the results from the DMRG-SCF method. We also take the advantage of the two-body density matrix obtained within MC-DMRG scheme and optimize geometry on the DMRG-SCF level. At last, we discuss possible ways of incorporating the dynamical correlation into the DMRG scheme which can lead to a modern multireference approach. (More information about one way towards this direction can be found at a poster of Ligu Kong from our group.)

Can Coupled-Cluster Methods Describe Conical Intersections?

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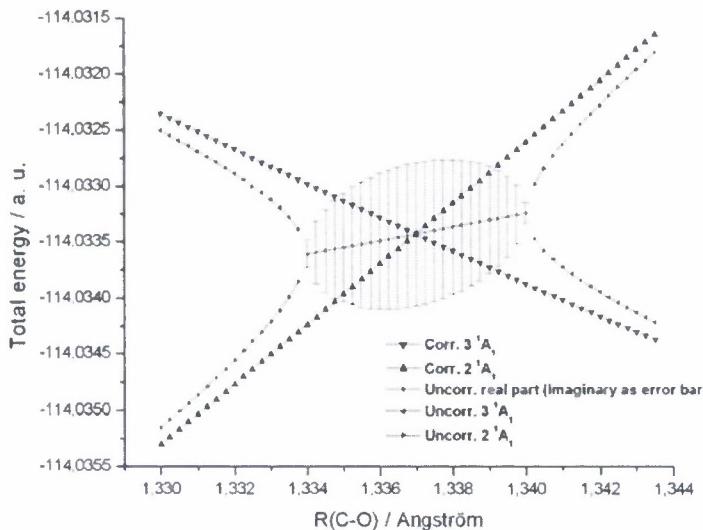
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The concept of the conical intersection (CoIn) between electronic states is of great importance for the understanding of radiationless ultrafast relaxation processes. A CoIn is the locus where two adiabatic potential energy surfaces become energetically degenerate. This can happen in F -2-dimensional subspaces (seams) of the F -dimensional space of nuclear configurations.

Inherently Hermitian methods like configuration interaction always give a qualitatively correct description of the topology near CoIns. For non-Hermitian methods such as coupled-cluster (including multi-reference coupled-cluster), however, this is by no means guaranteed as soon as the wave-function expansions are truncated. At intersections between states of the same spacial symmetry non-Hermitian coupling matrix elements occur. We will analyze the origin of these non-Hermitian contributions and their effects, *i.e.*, linear dependent eigenvectors and complex eigenvalues.

Numerical examples are given for conical intersections between two excited states calculated at the equation-of-motion coupled-cluster level. A simple method is discussed which allows physically meaningful potential energy surfaces to be extracted from the otherwise ill-behaved results.



Theoretical Investigations on the Hydrosilylation, Hydrocyanation, and Hydroamination of Ethene Catalyzed by Hydrido-Bridged Diplatinum Catalysts

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A detailed reaction mechanism of the catalytic cycles of the hydrosilylation, hydrocyanation and hydroamination of ethene catalyzed by hydrido-bridged diplatinum complexes was explored with the aid of electronic structure calculation techniques. The geometric, energetic and electronic properties of the relevant intermediates and transition state structures have been calculated. All crucial reaction steps encapsulated in the entire catalyzed courses have been scrutinized. Three critical steps were found to be the rate-determining steps of the catalytic cycles namely: (i) the hydride migration to the acceptor C atom of the coordinated ethene substrate, (ii) the reductive elimination of the final product and (iii) the oxidative addition process that regenerates the catalyst with the activation barriers amounted to 13.1, 16.5 and 13.3 kcal/mol for hydrosilylation, 7.1, 31.0 and 2.8 kcal/mol for hydrocyanation and 11.7, 39.7 and 39.0 kcal/mol for hydroamination reactions. The overall catalytic processes are exothermic, the predicted exothermicities being $-13.5(-8.0)$, $-16.1(-10.4)$ and $-38.8(-46.7)$ kcal/mol for the hydrosilylation, hydrocyanation and hydroamination of ethene, respectively at the B3LYP (CCSD(T)) levels of theory. According to the energetic span of the cycle called δE , which determines the frequency of the catalytic cycle, the catalytic efficiency of the hydrido-bridged diplatinum catalysts follows the trend: hydrocyanation \geq hydrosilylation $>$ hydroamination. This study seeks to extend further our understanding of the intricate structural and energetic details of the three catalytic processes.

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**HX Photochemistry on Water Particles: Electronic Structure
and ab Initio Quantum Molecular Dynamics**

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Acid dissolution of hydrogen halide molecules in liquid water to X^- and H_3O^+ ions belongs to the most fundamental reactions in chemistry. The acidic dissociation has been studied both theoretically and experimentally in the gas phase, in the bulk, on the ice surfaces and in the molecular clusters. Despite the great effort devoted to acidic dissociation molecular details of this process remains still somewhat controversial. Recently, we have found that the problem of acidic dissociation can be studied by means of photodissociation experiment [1]. It was concluded that HCl and HBr molecules dissociate in the ground state on the surface of large water cluster at the temperature of 100 K. After the subsequent photodissociation the charge-transfer-to-solvent (CTTS) state is reached leading to the formation of a neutral H_3O molecule. This metastable radical then decomposes into a H_2O and H detected in the experiment.

We have further studied $HX@(\text{H}_2\text{O})_n$ ($X = \text{F}, \text{Cl}, \text{Br}$) clusters by a combination of static electronic structure calculations and *ab initio* quantum molecular dynamical calculations. In particular, we have studied the structure of the clusters in the ground state, including the influence of quantum nuclear effects. We have calculated absorption spectra of various molecular clusters, starting either from intact HX or from a charge separated states. We have also investigated the electronic structure and relaxation in the excited state.

Static quantum chemical calculations can however not provide any information on the duration of the molecular processes. Our conclusions can also be driven by an early expectations or prejudice. It is therefore useful to solve dynamical equations for atomic nuclei to overcome these limitations, i.e. perform molecular dynamics calculations. We have explored the photodissociation dynamics using Full Multiple Spawning method [2]. This method is solving quantum equations of motion for atomic nuclei which is required since more than one electronic state is involved in the process. At the same time we solve the electronic Schrödinger equation on-the-fly.

Results of our calculations allow us to interpret the experiment. HF is shown to behave significantly differently than the other hydrogen halides. Some methodological aspects of the calculations are also discussed [3].

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[PII-31]

Nitrosation of Melatonin

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Melatonin is present in many organisms including many very primitive organisms. Humans produce it in the pineal gland and it plays a role in regulating the body clock. It has also been shown to act as a radical scavenger [1]. The antioxidant/prooxidant balance in the body is very complex and involves many competing reactions. The nitrosation of melatonin is one of the most important reactions in understanding melatonin's role in helping to regulate the antioxidant/prooxidant balance in the human body. Because these reactions occur in the body, it can be important to include solvent effects. Both implicit [2] and explicit [3] solvent calculations have been performed to determine the impact of solvent on the reaction profile. This also helps to determine the level of theory at which the solvent effects must be represented.

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[PII-32]

The Radical Character of the Acenes

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The nature of the acene ground state - its spin, singlet-triplet gap, and diradical character as a function of chain-length - is a question of ongoing theoretical and experimental interest with notable technological implications. Previous computational studies have given inconclusive answers to this challenging electronic structure problem. We present a detailed investigation of the acene series using high-level wavefunction theory. Our local ab-initio Density Matrix Renormalization Group algorithm allows the numerically exact (FCI) solution of the Schrödinger equation in a chosen 1-particle basis and active space for quasi-one-dimensional systems. It has enabled us to carry out Complete Active Space calculations on the acenes from naphthalene to dodecacene correlating the full pi-valence space. While we find that the ground-state is a singlet for all chain-lengths, examination of several measures of radical character, including the natural orbitals, effective number of unpaired electrons, and various correlation functions, suggests that the longer acene ground-states are polyradical in nature. This argues for a fruitful view of acenes as strongly interacting electronic systems.

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Singlet-Triplet Coupling in Photobiologically Relevant ChromophoresChristel M. Marian, Martin Kleinschmidt, Jörg Tatchen, and Susanne Salzmann*Heinrich Heine University, Düsseldorf, Düsseldorf, Germany*

Singlet-triplet coupling is an important issue in photochemistry, photobiology, and photomedicine. While a high triplet quantum yield is desirable for photosensitizers, rapid quenching of the T1 state is preferable for photoprotectors. Photophysical relaxation of an organic molecule after electronic excitation often involves dark transient states, i.e., intermediate singlet and triplet states not visible in absorption or emission. A prerequisite for the understanding of the underlying mechanisms is the knowledge of the excited states and their interactions. State-of-the-art quantum chemical methods can help to shine light on the cascade of relaxation processes. The combined density functional and configuration interaction method (DFT/MRCI) [1] has proven to yield high-quality electronic excitation spectra, even in cases where time-dependent density functional theory (TDDFT) fails as, e.g., in carotenes. Spin-orbit related properties are calculated using the SPOCK program package, developed in our laboratory [2-4]. Franck-Condon factors are computed for vibrational modes with the largest coordinate displacements [5]. Derivatives of spin-orbit coupling matrix elements, employed in a Herzberg-Teller-like expansion, are determined numerically [6]. By means of the above mentioned methods, we have investigated the electronic spectra and spin-orbit coupling of a variety of photobiologically relevant chromophores. Among these are flavins [7], psoralens [5], porphyrins [4], and carotenes [8]. In the case of psoralen, vibronic spin-orbit coupling between S1 and T1 states has to be invoked to explain the high triplet quantum yield in aqueous solution [6].

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[PII-34]

**Electroweak Molecular Quantum Mechanics:
Analytic Derivatives within One- and Two-Component Approaches**
Robert Berger, Guido Laubender, Sophie Nahrwold, and Jason L. Stuber

Within the unified theory of electromagnetic and weak interactions, intriguing phenomena that are absent in traditional quantum chemistry arise. Computationally, these effects which range from optical activity of achiral molecules over coupling between states of opposite parity in rotational spectra of diatomics to parity violating energy differences between non-identical mirror image molecules become accessible only within the framework of electroweak molecular quantum mechanics [1].

Here we present an avenue to the calculation of electroweak effects in molecular systems within one-component (non-relativistic) and two-component (quasi-relativistic) approaches. Analytic derivative techniques are exploited to calculate parity violating molecular properties which are at the forefront of fundamental research in molecular physics. The accurate prediction of these properties is of crucial importance for current attempts to measure molecular parity violation for the first time. In this presentation, we focus on the calculation of nuclear magnetic resonance frequency differences [2-4] as well as of vibrational frequency differences [5] between enantiomers and discuss possible molecular candidates for a successful measurement.

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[PII-35]

Theoretical Modeling of Vibrational Spectra
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Anharmonicities in molecular vibrations are highly sensitive to the potential energy surface. Variational methods can reach quantitative accuracy in modeling anharmonic spectra; however, their effectiveness is limited by the quality of the PES. A form is discussed which contains full nuclear permutational symmetry; this both reduces the number of data points required for fitting, and avoids artifactual errors from an unsymmetrized PES. Preliminary results for the diazomethane molecule will also be discussed.

Introducing a Consistent Relativistic Description into Simulations: Combining Second Order Douglas-Kroll-Hess Theory with First-Principles Simulations

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Up to now simulations on systems containing heavy atoms where the electronic structure is calculated on the fly are limited mainly to relativistic pseudopotentials for the description of relativistic phenomena. This description depends on relativistic all-electron calculations as reference and could yield inaccurate results for molecular properties being probed at the relativistic nuclei. The wide application of pseudopotentials in simulations originates in the expansion of the wavefunction in plane waves. One way to replace the pseudopotential by a cost efficient orbital representation is the Gaussian and augmented plane wave method (GAPW) [1,2]. This approach is derived from the projector augmented-wave method [3]. The GAPW method is already implemented in the program package CP2K [4]. It describes the core electrons with a Gaussian type basis set, while the valence density is expanded into plane waves.

The scalar-relativistic Douglas-Kroll-Hess (DKH) method [5,6] is well suited to introduce a consistent relativistic description into simulations. It is computational efficient in its lowest orders as a necessity to converge results sufficiently for molecular properties. This means with regard to benchmark purposes that it is systematically improvable [7,8]. Furthermore it needs only information which is already available in standard electronic structure programs, except for \mathbf{pVp} matrix elements. First implementations of the DKH method in a program applying hybrid Hamiltonians with periodic boundary conditions were successful [9]. Analytic gradients [10], that are naturally required in simulations, must be implemented in the GAPW framework.

As a first step, \mathbf{pVp} integrals have been implemented in the CP2K code, so that the DKH module for calculations up to fourth order is currently attached to the SCF routine [11]. The program is intended for dynamical systems which contain heavy elements, e.g. ionic liquids with lanthanides as anions.

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[PlI-37]

UNO-CAS: A Poor Man's Approach to Electron Correlation that Works

Jane Zhou

DuPont

The unrestricted natural orbital – complete active space (UNO-CAS) method for quantum chemistry calculation is an inexpensive alternative to the complete active space – self-consistent-field (CAS-SCF) theory. UNO-CAS was developed in Professor Pulay's lab in late 1980s when computing resources were scarce and large-scale CAS-SCF calculations were prohibitively expensive. As a tribute to Professor Peter Pulay on this special occasion, this poster will summarize applications of UNO-CAS of some strongly correlated systems, and some of the results of these applications were experimentally confirmed by several scientists in other universities years later. The examples demonstrate that one of Professor Pulay's genius contribution in solving quantum mechanical problems.

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[PlI-38]

Hydrogen Abstracted Adenine-Thymine Radicals With Remarkable Transferable Properties

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The formation of radicals on DNA bases through various pathways can lead to harmful structural alterations. Such processes are of interest for preventing alteration of healthy DNA, and conversely to develop more refined methods for inhibiting the replication of unwanted mutagenic DNA. In the present work we explore theoretically the energetic and structural properties of the nine possible neutral radicals formed via hydrogen abstraction from the adenine-thymine base pair. The lowest energy radical is formed by loss of a hydrogen atom from the methyl group of thymine. The next lowest energy radicals, lying 8 and 9 kcal/mol higher than the global minimum, are those in which hydrogens are removed from the two nitrogens that would join the base pair to 2-deoxyribose in double stranded DNA. The other six radicals lie between 16 and 32 kcal/mol higher in energy. Unlike the guanine-cytosine base pair, A-T exhibits only minor structural changes upon hydrogen abstraction, with all A-T derived radicals maintaining planarity. Moreover, the energetic ordering for the radicals of the two isolated bases (adenine and thymine) is preserved upon formation of the base pair, though with a wider spread of energies. Even more significantly, the energetic interleaving of the (A-H)'-T and A-(T-H)' radicals is correctly predicted from the X-H bond dissociation energies of the isolated adenine and thymine. This suggests that for small DNA model systems the properties of isolated nucleic acid bases may be more transferable to larger DNA subunits than previously imagined.

**Hybrid *ab Initio* Valence Bond/Molecular Mechanics (VB/MM),
A New Method for Calculations of Biochemical Systems**

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The growing demand for realistic methods that would calculate chemical reactions in biological systems resulted with the development of hybrid quantum mechanical (QM) molecular mechanical (MM) schemes. Recent years have proven schemes that are based on concepts from valence bond (VB) methodology, to be beneficial for the description of enzyme catalysis and reactivity. The development of a new hybrid (QM/MM) method where the QM part is treated by *ab-initio* Valence Bond (VB) theory will be presented [1]. This VB/MM method has the advantages of Empirical VB (EVB) methodology but should provide better accuracy and does not rely on empirical parameterization for the quantum part. The validity of the method will be shown to be successful in several examples.

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Dynamic Hyperpolarizabilities and Raman Intensities

Calculated within Coupled-Cluster Theory

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As the highly accurate calculation of molecular energies becomes more routine with the widespread application of coupled-cluster methods (CC), there is a growing need to increase the accuracy and also the range of properties which can be derived from these energies. Currently, analytical second derivatives for CC have been implemented in a limited number of quantum chemistry packages. Such an implementation exists in ACES II for the calculation of electrical, magnetic and geometric derivatives, providing properties such as static and dynamic polarizabilities, magnetizabilities, NMR shifts, infrared intensities and harmonic force constants. Here we present a preliminary report on the development of third-order properties building on the existing second-order framework in ACES II. In particular we focus on the calculation of dynamic hyperpolarizabilities and Raman intensities, and their evaluation in conjunction with the general coupled-cluster package MRCC. Some demonstrative examples are presented.

Wavefunction-Based Correlated *ab Initio* Method for Metals

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Ab initio wavefunction-based correlation methods are desirable for extended systems, because they yield a systematically improvable method for the many-body ground-state properties. One of these methods which can be applied to solids is the method of increments [1]. It combines Hartree-Fock calculations for periodic systems with correlation calculations on the corresponding finite embedded cluster, where the total correlation energy per unit cell of a solid is written in terms of interactions of increasing complexity among the electrons assigned to localized orbitals comprising the solid under consideration. The method of increments has been applied to a variety of systems from strongly bound ionic or covalent systems to weakly bound van der Waals solids, from large molecules over polymers to three-dimensional solids, from weakly correlated systems to strongly correlated ones [2]. All this applications in common is the occurrence of an energy gap between occupied and virtual orbitals, or in the language of the solid state physics between valence and conduction bands. A generalization is possible for metals, where two major problems have to be faced: First, a straight-forward localization of the orbitals is not possible, localized entities have to be generated via an embedding scheme. Second is the difference between bulk metals and metal clusters. Within an infinite metal there is a homogeneous distribution of the conduction electrons, whereas in a cluster the charge will move to the surface. To fix these problems it is necessary to construct an embedding for the finite entities in such a way that the metallic character is simulated properly. For this purpose we suggest an embedding which has itself no metallic character but can mimic the metal in the internal region, where the atoms are correlated [3]. Results obtained for the group II metals show that the method of increments is a robust method for the calculation of correlation energies in metallic systems.

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[PII-42]

**Inexpensive Methods for Thermodynamical Calculations
of Systems with Multiple Internal Rotors**

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Thanks to the pioneering work of Peter Pulay and others, computational quantum chemistry has seen a rapid development during the last decades. Thermodynamic quantities can today be calculated at an accuracy that for many systems rivals the best experiments. As the advances in electronic structure theory continue, the use of the harmonic oscillator approximation for treating nuclear motion becomes more and more of a limiting factor. At elevated temperatures, many molecular systems exhibit large amplitude motions that are anharmonic in character. The nuclear motions of weakly bound systems, such as molecular complexes and transition states, are often strongly anharmonic already below room temperature. Internal rotation is without doubt the most important of the anharmonic motions that cause errors in thermochemical calculations. This presentation introduces two general methods for treating the thermodynamics of internal rotation. The two methods allow thermodynamical quantities to be calculated from a molecular Hessian obtained at one nuclear geometry with a minimum amount of computational effort. Both methods consider the mixing between rotors within each internal rotation mode. In addition, the mixing between internal rotation and other types of vibrational motion is explicitly accounted for. The performance of the two new methods for thermochemical calculations has been evaluated for molecules with several internal rotors by comparison with experimental data and accurate calculations with explicit consideration of the coupling between internal rotors. When used with the one-dimensional rotor partition function of Pitzer and Gwinn, both methods are found to perform well also for complex systems. Thus, the new methods provide computationally inexpensive alternatives for accurate treatment of molecular systems with multiple hindered rotors.

[PII-43]

**Efficient Evaluation of Analytic Second Derivatives in Hybrid Density
Functional Theory for Periodic Non-Conducting Systems**

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We report an efficient method for the analytic second derivatives of energy with respect to in-phase ($k = 0$) nuclear coordinate displacements within Hartree–Fock and Kohn–Sham density functional theories, using Gaussian orbitals and periodic boundary conditions. The use of the atomic orbital formulation for all computationally challenging parts allows us to adapt the direct space fast multipole method for the Coulomb-type infinite summations. Our implementation also exploits the local character of the exact Hartree-Fock exchange and density functional exchange-correlation contributions by using extensive screening and fast numerical quadratures. We benchmark one-, two-, and three-dimensional systems to illustrate the capabilities of our method.

Development and Applications of Multireference Density Functional TheoryKazuto Nakata,^a Takeshi Ukai,^a Shusuke Yamanaka,^aToshikazu Takada,^{b,c} and Kizashi Yamaguchi,^{a,c}^a Department of Chemistry, Graduate School of Science, Osaka University

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Although almost all of electronic structures of the ground-and-excited states can be routinely accessible by restricted Kohn-Sham (KS) DFT and time-dependent (TD) DFT, the states with strong static correlation effects are beyond the scope of KS- and TD-DFTs. To work out this problem without using broken-symmetry solutions, a new class of electronic structure theory, multireference density functional theory (MR-DFT), has been developed by several groups [1]. We have also developed several versions of MR-DFT [2,3]. In particular, our recent MR-DFT approaches are based on the effective CI equations involved with effective DFT correlation field and extended for the excited states, which corresponds to the MR-DFT version [3] of subspace DFT [4]. In this study, we apply these MR-DFT approaches based on complete-active-space (CAS) CI and CASSCF wavefunctions for ground-and-excited states of organic-and-inorganic magnetic compounds. The computational results are discussed in the relation with the experimental results and hybrid-DFT's results.

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Visualisation and Properties of the First-Order Current DensityGábor Magyarlalvi

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The first order current density induced by a magnetic field in a molecular electron density can be quite useful in characterizing molecular properties. Many studies have linked aromaticity and antiaromaticity with ring currents forming in molecules. Recently Jusélius et al. have implemented [1] a method to compute the first-order current density using gauge including atomic orbital (GIAO) basis sets. We are using similar calculations to obtain molecular current density distributions. These current density fields can be quite complex, but visualization techniques developed for medical imaging can be helpful in extracting and emphasizing relevant information from the data sets. Plotting other quantities derived from the computed current density can also provide aesthetically and intellectually stimulating pictures of molecular electron structures.

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[PII-46]

On the Mechanism of the Interchanging Axial and Equatorial

Ligands in Pentavalent Phosphor Compounds

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The ligands of pentavalent phosphor compounds with two synchronized bending motions (a pair of ligands in apical and a pair of ligands in equatorial positions) can exchange in the trigonal bipyramidal structures through a tetragonal pyramid transition state (TS) (Berry pseudorotation, **BPR**). A similar change can take place by a turnstile rotation which also result the interconversion of enantiomers, where an apical and an equatorial bond rotate relative to the other three bonds. The mechanism in small phosphoranes with H, F, CH₃, OH, OCH₃ and Phe ligands were studied at the level of *ab initio* methods by using HF and DFT methods. The geometry, the electronic properties and the change in d-orbitals were characterized in the **TSs** and along the reaction paths (**RP**s). The **RP**s were calculated by **DDRP** (Dynamically Defined Reaction Path) method coupled to Gaussian98, which can be considered as a global method to find the **RP**s or intrinsic reaction coordinates (**IRC**s). The barrier heights of the two rearrangements were compared to each other at different ligands.

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[PII-47]

Fictitious Hydrogen Atoms as a Versatile Tool to Investigate Substituent Effects

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Considerable research efforts in organic chemistry has been aimed at understanding the electronic and steric properties of substituents. One of the most serious difficulties, besides experimental limitations, is that a substituent effect is the resultant of a subtle interplay between inductive components, resonance components, and other non-electronic contributions. The key idea to our approach is the use of fictitious nuclear charges, born by hydrogen atoms H*. These H* atoms have no resonance component but their inductive power is adjustable. This enables us (*i*) to study the influence on a given substrate, for any physical or reactional magnitude. A striking application to the reference Diels-Alder reaction revealed a non-FMO behaviour for H*-substituted butadiene and provide an interpretation for some surprising regioselectivities. (*ii*) to construct a partition of electronic substituent effects into inductive and resonance contributions. The H* method also sheds new lights on more fundamental questions, such as the additivity of inductive effects or transmission mechanisms.

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**Efficient Strategies for the Linear-Scaling Calculation
of Moller-Plesset Correlation Energies**Daniel Lambrecht, Bernd Doser, and Christian Ochsenfeld*Institut für Physikalische und Theoretische Chemie, Universität Tübingen
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The selection of numerically significant integrals is of central importance in AO-based formulations of quantum chemistry. A prominent example is the use of the powerful Schwarz integral bound [1], which led to the breakthrough of direct SCF methods. Although the Schwarz bounds are widely employed and accepted, there remains room for improvement [2,3]. Recently, we presented multipole-based integral estimates (MBIE) [3], which account for the first time rigorously for the $1/R$ distance decay between the charge distributions of two-electron integrals. This does not only allow for more efficient screening in the context of (linear-scaling) SCF methods, but, most importantly, MBIE is suited to exploit the strong distance decay of electron-correlation effects of at least $1/R^{**4}$ in AO-based formulations of MP2 theory [4,5]. In this way, the MBIE bounds can be used to reduce the number of transformed Coulomb integrals within the AO-MP2 method [6,7] rigorously from $O(N^{**2})$ to $O(N)$, while preserving accuracy and reliability [4]. Here, we present recent progress in attaining efficient and linear-scaling reformulations of MP2 theory. Also, the importance of rigorous integral bounds is discussed by theoretical and numerical arguments.

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[PII-49]

Electron Spin-Spin Coupling within an MRCI-treatment: First Results

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Electron spin-spin coupling occurs in $S \geq 1$ systems due to an interaction of unpaired electrons. Theoretical description is highly demanding: The spin-spin operator in its two-component Breit-Pauli formulation consists of five terms. Consequently, we have to consider an increased number of integrals as compared to nonrelativistic electron interaction; additionally, the effect of electron spin has to be considered. The number of implementations, especially on a sophisticated *ab initio* level, is therefore limited. Recent work includes CASSCF and MCSCF as well as DFT approaches.

We present a perturbative spin-spin-coupling implementation on top of the selective MRCI treatment of Grimme and Waletzke [1]. Thereby, electron correlation is considered on a high level, accounting for static as well as dynamical interaction. The spin-spin approach is implemented in the SPin-Orbit Coupling Kit [2,3,4] which was developed and applied in our group. The algorithm employed in the spin-orbit case based upon the work of Wetmore and Segal [5] could be extended and applied to the spin-spin case, thus allowing for an efficient evaluation of the spin-spin interaction.

First results for the test cases O_2 and CH_2 are presented.

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[PII-50]

Calculating Photoelectron Angular Distributions from EOM-IP-CCSD Dyson Orbitals

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We present the application of Dyson orbitals for the calculation of photoelectron angular distributions (PADs) obtained in photoionization experiments. Dyson orbitals represent the overlap between an N -electron molecular wave function and the $N-1/N+1$ electron wave function of the corresponding cation/anion. Their implementation within the high-level EOM-IP/EA-CCSD *ab initio* methods allows the calculation of individual contributions from each excited state to the experimental PAD. It is thus possible to determine the states involved in the photoionization process. We focus on the photodissociation of the NO dimer, for which the experimental PAD shows a pronounced change as the molecule evolves on the potential energy surface.¹

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A New Quantum Mechanical Hybrid Scheme for Local Correlation Methods

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The accurate treatment of electron correlation is fundamental for a quantitative description of chemical reactions. The use of *ab initio* correlation methods, although offering a systematic solution to this problem, is impeded by the higher order scaling of computational effort with increasing molecular size. These methods, in their conventional implementations, can only be routinely applied to systems of up to 20 atoms. Local correlation treatments, as originally proposed by Pulay and first implemented by Pulay and Saebo, employ local orbital spaces to restrict the number of excited configurations in the wavefunction. The occupied orbitals are localized using standard procedures, while the virtual space is spanned by non-orthogonal projected atomic orbitals (PAOs). By fully exploiting the locality, our group has achieved linear scaling of the computational effort with molecular size for all standard single-reference methods. This work offers an extension to this treatment by allowing different levels of correlation to be used in different part of the molecular system. This is achieved by classifying orbital pairs according to regions of different chemical interest. Since both occupied and virtual space are local, the orbital pairs (and respective domains) are implicitly subsections of our system. There is no need to build model systems and cut bonds, the hybrid scheme can be applied in a simple run. Test calculations have been performed on a series of reactions, including an enzymatic system. The hydrogen bonding energy of water to aminoacid chains has also been studied, and both test cases show promising results, even in comparison to other popular coupling schemes. First results for frequency calculations are also shown for small water and ammonia clusters.

[PII-52]

**Cyanides and Isocyanides of First-Row Transition Metals:
Molecular Structure, Bonding, and Isomerization Barriers**

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Cyanides and isocyanides of first-row transition metals M(CN) (M=Sc-Zn) are investigated with quantum chemistry techniques, providing predictions for their molecular properties. A careful analysis of the competition between cyanide and isocyanide isomers along the transition series has been carried out. In agreement with the experimental observations, late transition metals (Co-Zn) clearly prefer a cyanide arrangement.^[2,3] On the other hand, early transition metals (Sc-Fe), with the only exception of the Cr(CN) system, favor the isocyanide isomer. The theoretical calculations predict the following unknown isocyanides: ScNC(3DLTA), TiNC(4PHI), VNC(5DLTA), and MnNC(7SG+), and the CrCN(6SG+) cyanide, and agree with the experimental observation of FeNC(6DLTA).² First-row transition metal cyanides and isocyanides are predicted to have relatively large dissociation energies with values within the range 80-101 kcal mol⁻¹, except Zn(CN) which has a dissociation energy around 50-55 kcal mol⁻¹, and low isomerization barriers. A detail analysis of the bonding has been carried out employing the topological analysis of the charge density and an energy decomposition analysis.

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**The SQM Force Field Method applied to the Interpretation
of Vibrational Spectra Measured in Condensed Phases**

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Due to the availability of fast and reliable computers it is nowadays possible to do ab initio and density functional calculations on relative large molecules. Using such methods, one can calculate the molecular force field, from which vibrational frequencies and IR and Raman intensities can be obtained. However, the calculated frequencies usually differ from the observed ones because of anharmonicity and approximations in the quantum mechanical formalism. As Pulay has shown [1], one can minimize these deviations according to the SQM force field method, i.e. by scaling of the quantum mechanical force field in internal coordinate representation. In this work we describe our experience of applying SQM force fields to the calculation of vibrational spectra measured in condensed phases, e.g. for sodium acetate [2], methylthiobenzonitrile [3] and some isochromanone derivatives [4]. The scale factor calculations have been done with the program MOLVIB, which was modified not long ago [5] to make it possible to do scale factor calculations by the Pulay method. The agreement between the calculated and observed frequencies was improved by a least squares adjustment of selected scale factors. This is justified by the need to allow for variations in the effective force field due to the effects of environment, e.g. presence of counter ions, solvent, or condensed phase medium surrounding the molecule.

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[PII-54]

The Oxyheme Complexes of P450cam: A QM/MM Study

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The substrate bound heme-O₂ complexes (ferrous dioxygen, S4 and ferric peroxy, S5) of P450cam (CYP101) have been studied by combined quantum mechanical / molecular mechanical (QM/MM) calculations. The oxyheme (without side chain) is treated with density functional theory and the protein/solvent environment by the CHARMM22 force field. The B3LYP/CHARMM calculations are found to give reasonable descriptions of the oxyheme complexes. An open-shell singlet is predicted to be the ground state for S4 with small energy separations to the excited states. This result is consistent with previous experimental and QM studies. Comparisons with analogous calculations on the isolated QM system in the gas phase show that the protein/solvent environment reduces the open-shell singlet-quintet energy gap which should facilitate the spin inversion upon the binding of the atmospheric oxygen. An intact ferric peroxy complex S5 is found only in the doublet state whereas the quartet and sextet states dissociate upon QM/MM optimization (uncoupling).

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[PII-55]

The Equilibrium Structure of Ferrocene

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The structural parameters of ferrocene in its eclipsed (equilibrium) and staggered (saddle point) conformations have been determined using analytic CCSD(T) gradient calculations as available in the parallel version of ACES II. The results are compared with the experimentally determined geometries, previous theoretical studies as well as DFT calculations.

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[PII-56]

**An Evaluation of OM2/GUGA-MRCI Performance
in Excited State Geometry Optimizations**

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By studying over a hundred electronically excited states of 32 molecules, the recently developed OM2/GUGA-MRCI approach was systematically evaluated for its performance in excited state geometry optimization. Four types of bond lengths (carbon-carbon, carbon-hydrogen, carbon-nitrogen, and double carbon-oxygen) and bond angles obtained from semiempirical geometry optimization were compared with CASSCF geometries from the literature that have been obtained using the same active spaces and symmetric constraints. Adiabatic excitation energies were also compared with references of experimental and CASPT2 results. A set of parallel calculations employing TDDFT at B3LYP/TZVP level was performed to supplement these data. The statistical evaluations show that the OM2/GUGA-MRCI approach is not only a fast computational method but also a generally promising tool to study adiabatic properties of excited states. Some cases where OM2/GUGA-MRCI does not reproduce the nonplanar excited reference geometries are discussed and suggestions are made for future parameterizations and improvements. The present work serves as validation of the OM2/GUGA-MRCI approach for studying large biological molecules which undergo photochemical processes.

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Accurate Ground and Excited State Studies for Molecular Systems of Biological Interest

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Excited state calculations for biological systems have been of great interest for many years. Until recently they have been mainly limited to evaluation of excitation energies for relatively rigid molecules with geometry structures assumed unchanged upon electronic excitation. But most real systems of biological interest have a flexible structure, and such assumptions can no longer stand. It has been only recently that advances in quantum mechanic calculations, in particular Time-Dependent Density Functional Theory (TD-DFT) [2] made an important progress toward accurate studies of excited states for larger systems. It is now possible to perform full geometry optimizations at TD-DFT level in order to obtain molecular or complex structure in excited state. Such approach combined with DFT/TD-DFT vibrational frequency calculations and evaluation of energies at correlated Coupled Cluster (CCSD(T), EOM-CCSD) level can lead to highly accurate results for flexible molecular systems. Anisole and its complexes [2] are interesting examples for ground and excited state studies of weakly bounded molecular systems. Their structure can be stabilized by several relatively balanced inter- and intra-molecular interactions (classical hydrogen bond with anisole molecule acting as proton donor/acceptor, hydrogen bond and long range dispersion/VdW forces) leading to many possible geometries. In this work various theoretical approaches from density functional theory (DFT, TD-DFT) to accurate correlated methods (CCSD(T), EOM-CCSD) have been used to address issues such as molecule and complex structures, vibrational frequencies, interaction energies and photoelectron spectra [3].

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[PII-58]

**Self-Consistent Combination of the Three-Dimensional RISM
Theory of Molecular Solvation with Analytical Gradients
and the Amsterdam Density Functional Package**

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Nowadays, the self-consistent field combination of KS-DFT electronic structure methods and statistical-mechanical 3D-RISM theory of molecular liquids [1] represents one of the most efficient ways, in terms of accuracy and computational cost, for predictive description of solvent effects on structure and functions of solutes. It treats a solute molecule fully in a three-dimensional manner, whereas orientational averaging around interaction sites is applied to solvent molecules. This yields the three-dimensional classical density distributions of interaction sites of solvent molecules around a solute particle of arbitrary shape. This method supplemented by calculation of analytical gradients [2] allows one to calculate the properties, optimize geometries, search for transition states and reaction coordinates. In this work we present a detailed evaluation of the new self-consistent field KS-DFT/3D-RISM method which has been implemented in the ADF package. We performed several characteristic tasks of computational chemistry: the free energies, energies of taumetrization for a number of organic compounds; water distribution inside the carbon nanotubes; the activation parameters and coordinates of SN2 reactions in aqueous solvent; and those of SN2 reactions in the inner part of a carbon nanotube. The results are similar to those obtained by continuum solvation approaches, and moreover, are at the level of ab-initio QM/MD methods [3]. We also discuss the timings in comparison to the COSMO method.

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[PII-59]

In Search of Definitive IR Signatures of the Elusive NCCO Radical

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Previous experimental assignments of the fundamental vibrational frequencies of NCCO have been brought into question by subsequent unsuccessful attempts to observe IR signatures of this radical at these frequencies. Here we compute the fundamental vibrational frequencies by applying second-order vibrational perturbation theory (VPT2) to the complete quartic force field computed at the all-electron (AE) coupled cluster singles, doubles, and perturbative triples level [CCSD(T)] with the correlation-consistent, polarized core-valence quadruple-zeta (cc-pCVQZ) basis set, which has tight functions to correctly describe core correlation. The AE-CCSD(T)/cc-pCVQZ geometric parameters, $r_e(\text{N-C}) = 1.1623 \text{ \AA}$, $r_e(\text{C-C}) = 1.4370 \text{ \AA}$, $r_e(\text{C-O}) = 1.1758 \text{ \AA}$, $\theta_e(\text{N-C-C}) = 168.55^\circ$, $\theta_e(\text{C-C-O}) = 132.22^\circ$, yield rotational constants in excellent agreement with microwave spectroscopic measurements. Our CCSD(T)/cc-pCVQZ values of the characteristic stretching frequencies ν_1 and ν_2 are 2171 cm^{-1} and 1898 cm^{-1} , respectively, in stark contrast to the experimentally-derived values of 2093 cm^{-1} and 1774 cm^{-1} . Finally we perform Focal-Point extrapolations using correlation-consistent basis sets cc-pVXZ ($X = \text{D,T,Q,5,6}$) and electron correlation treatments as extensive as full coupled cluster singles, doubles, and triples (CCSDT) with perturbative accounting of quadruple excitations [CCSDT(Q)] determine the vibrationless barrier to linearity of NCCO and the dissociation energy (D_0) of $\text{NCCO} \rightarrow \text{NC} + \text{CO}$.

[PII-60]

Spectroscopic properties of InN in $\text{X}^3\Sigma^-$ and $^3\Pi$ states.

Comparison of MRDCI and DK-CCSD(T) methods.

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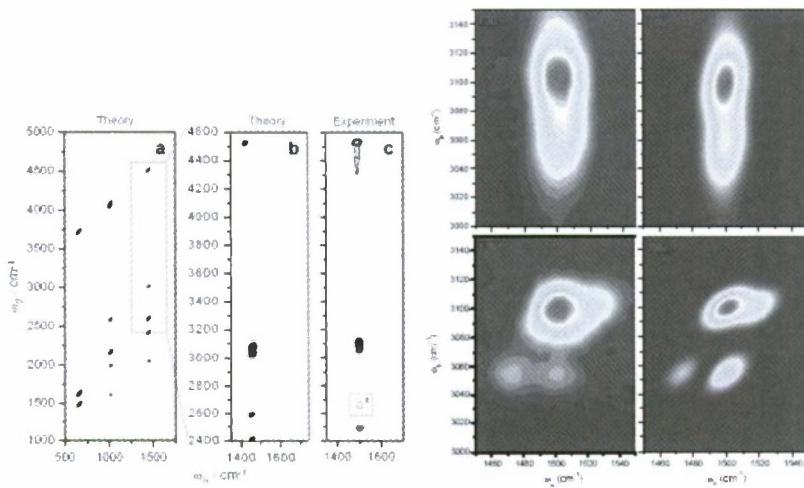
Spectroscopic constants of the two lowest states of the InN molecule, the $\text{X}^3\Sigma^-$ ground and the $^3\Pi$ excited state were calculated using the coupled cluster model with single and double excitations with the restricted open-shell Hartree Fock reference (ROHF-CCSD) and perturbative triples (CCSD(T)), complete active space second-order perturbation theory (CASPT2) and multireference configuration interaction (MRDCI) methods. Relativistic pseudopotentials (for MRDCI) and atomic natural orbital basis set suitable for treating spin-orbit and scalar relativistic effects - ANO-RCC (for CCSD(T), CASPT2 and CASPT2/RASSI-SO) were used. The accuracy of different methods was compared correlating up to 26 valence and core-valence electrons of N and In atoms.

Benzene, Fermi Resonances and DOVE-FWM Spectroscopy

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DOVE-FWM (Doubly vibrationally enhanced four wave mixing) spectroscopy is a form of two-dimensional coherent spectroscopy that measures both vibrational-vibrational and electronic-vibrational coupling simultaneously. It is being developed as a powerful analytical technique for biomolecules [1]. Yet in order to reach its full potential for structural and compositional analysis, a better understanding of the factors that contribute to experimental spectra is required. Perturbation theory, DFT calculations of third anharmonic coefficients and derivatives of dipole moments/polarizability of the molecule, combined with non-linear optical theory, were used to simulate DOVE-FWM spectra. We show that this is able to explain and predict the presence and identity of important spectral features and explain elements of the lineshape. The technique was applied to benzene, benzene derivatives and various amino acids. In particular, Fermi resonances in benzene shows characteristic spectral pattern with different laser pulse ordering [2]. The possibility of structure determination from 2D-IR spectra has also been also explored and preliminary results will be presented.



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[PII-62]

The RMP2-F12 Method for an Accurate Treatment of Open-Shell Molecules

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The RMP2 [1] method is a spin-contamination free analog of MP2 theory for restricted open shell reference functions. In this poster its explicitly correlated variant DF-RMP2-F12 is described. This method was recently developed in an orbital invariant form (which allows application with localized orbitals) based on prior DF-LMP2-F12 work [2]. First results are shown.

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[PII-63]

Internally-Contracted Multireference Coupled Cluster Method & Computer Aided Implementation

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Equation of Motion Coupled Cluster (EOM-CC) and Similarity Transformed Equation of Motion Coupled Cluster (STEOM-CC) have seen many successful applications to open-shell excited states. Their main drawback is that they require a ground state or parent state that is well described at the single reference level.

In another poster by Ondrej Demel from our group, the generalization of EOM-CC theory to a state selective internally contracted multireference CC theory (SS-EOMCC) is described. This approach requires the diagonalization of a transformed Hamiltonian over a space of active + singly excited determinants, and the size of this diagonalization step limits the applicability of this approach.

In this poster we discuss the use of an additional transformation, as in STEOM, such that the transformed Hamiltonian $\hat{G} = \left\{ e^{\hat{s}} \right\}^{-1} e^{-\hat{r}} \hat{H} e^{\hat{r}} \left\{ e^{\hat{s}} \right\}$ can be diagonalized over a space of active determinants only. This efficient approach opens up the possibility of applications to systems that require a very large active space, e.g. of the order of 100,000 determinants for the description of transition metal compounds. The approach is spin-adapted, state-selective, employs Brueckner orbitals to define the reference state, and free from the intruder state problem. In the future we plan to combine the present inclusion of dynamical correlation with Density Matrix Renormalization Group diagonalization procedures (see the poster on DMRG by Dominika Zgid from our group).

We also discuss the use of automatic derivation of spin-adapted unitary group equations and automatic code generation using programs written in Python. Other work in progress concerns an analogous internally contracted MRCC based on an alternative definition of normal-order. This new normal-order enables more suitable approximations to equations defining cluster amplitudes, than in the native approach.

**Spatial Partitioning of Electron Correlation Contributions
to the Activation Energy of Hydrogen Transfer Reactions**

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Recent studies of the energetics of hydrogen transfer reactions¹⁻⁵ have resulted in semiempirical models that attempt to rationalise barrier heights in terms of properties of reactants, and to provide a means to estimate barrier heights. We have attempted to extend this analysis by examining explicitly the role of electron correlation. Starting with symmetric reactions of the type:



where $X = \text{CH}_3$, NH_2 , OH , F , Cl , OOH , and ONH_2 , calculations were carried out at the RCCSD/aug-cc-pVDZ//RHF/aug-cc-pVDZ level of theory. After optimising the transition state and the reactant structure, the orbitals were assigned to parts of the molecule, $X-H$, X^\bullet , and an extra set of orbitals were treated as reacting orbitals, the orbitals whose localization changes during the reaction. To achieve this, as a first step, after the RHF optimization the orbitals were localized (Boys localization). These then were assigned to the above groups. Singlet and pair contributions to the correlation energy were summed up into six partitions, each describing interactions between the above three groups. Using this partitioning, it can be concluded which parts of the correlation energy increase, and which parts decrease the barrier height of the above reaction. A relatively simple scheme of orbital changes can be used to describe the reaction. The results may also be used to predict contributions of fragments in asymmetric reactions.

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[PII-65]

**Retaining the Excitation Degree Perturbation Theory for Multi-Configuration
Electronic Structure Cases: Concept, Performance, Problems, Solutions**

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Retaining the Excitation degree Perturbation Theory (RE-PT) [1] is a new and general method which fulfils all properties of a well defined theory in *ab initio* quantum chemistry. That is, it is strictly size-consistent, unitary-invariant and systematically-improvable, like Moller-Plesset (MP) perturbation theory and Coupled Cluster (CC) theory. Furthermore, it seems to fill the gap between these two standard approaches.

RE-PT belongs to the class of Rayleigh-Schrödinger perturbation theories. It is derived from the well known concept of doubly-occupied, active, and virtual orbital spaces. The unperturbed Hamiltonian contains all contributions of the second quantization Hamiltonian which retain the number of electrons in these orbital spaces. As this Hamiltonian is Retaining the Excitation degree (RE) the method is named RE-PT.

We present results of a multi-reference variant of RE-PT. We demonstrate that the concept leads straightforwardly to a generalised Van Vleck PT approach, that fulfils all properties of a well defined Quantum Chemical method. The states in the reference space are described on equal footing which allows for a unbiased optimisation of several electronic states as e.g. required for a proper description of conical intersections. For small reference spaces with obvious choices for active orbitals this theory shows excellent convergence of calculated electronic energies with increasing order of perturbation theory. However, more extended active orbital spaces give rise to intruder states which deteriorate or even spoil convergence of the perturbation series. We indicate possibilities to retain convergence for such cases.

Even though in the lowest orders of RE-PT scale as n^6 with the system size, the formal simplicity of the perturbation theoretical approach allows for very efficient implementations. We discuss strategies, which allow to apply this approach to extended systems like iron-protoporphyrin based enzymes.

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[PII-66]

Photoelectron Spectra from Wave Packet Dynamics

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Franck-Condon factors for photoelectron spectra can be computed from: (1) the overlap between initial and target vibrational wave functions; and (2) Fourier transform of a wave packet time autocorrelation function. These techniques were implemented in the new spectra modeling software using harmonic well approximation and full quantum mechanical treatment. The photoelectron spectrum of N_3 was modeled using *ab initio* potential energy surfaces of the cation electronic states. Anharmonic effects are discussed.

[PlI-67]

**Molecular Electric Properties for GUGA-Based
Second-Order Generalized Van Vleck Perturbation Theory**

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The recently developed, multireference, second-order Generalized Van Vleck Perturbation Theory (GVVPT2) method has been modified to incorporate use of the Graphical Unitary Group Approach (GUGA) to calculate the Hamiltonian matrix elements in the basis of Gelfand-Tsetlin state functions. Using the GUGA scheme together with the macroconfiguration technique, the modified version of GVVPT2 is computationally more efficient than previous variants. Moreover, the facile computation of one particle density and transition density matrices in the GUGA formalism is exploited.

In the present work, one-electron molecular properties (specifically, electric multipole moments up to hexadecapoles) of a few test molecules, obtained based on an expectation value formalism, are presented. Both spherical- and Cartesian-tensor multipole moments can be evaluated relative to an arbitrary origin, although the center-of -mass frame is the preferred choice for both neutral and charged species. The effects of relaxation of the MCSCF optimized orbitals due to the electric field potential were assumed to be negligible in this implementation.

Keywords: GVVPT2, multireference perturbation theory, response properties, multipole moments.

[PlI-68]

Electron Pair Localization Function: Towards a Theoretical Electrophilic Scale

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Electrophilic amination is an appealing synthetic strategy to construct carbon-nitrogen bonds. We explore the use of the quantum Monte Carlo method and a proposed variant of the electron-pair localization function the electron-pair localization function density as a measure of the nucleophilicity of nitrogen lone-pairs as a possible screening procedure for electrophilic reagents.

Keywords: electron-pair localization function, electron localization function, electrophilic amination, quantum Monte Carlo, chemical reactivity.

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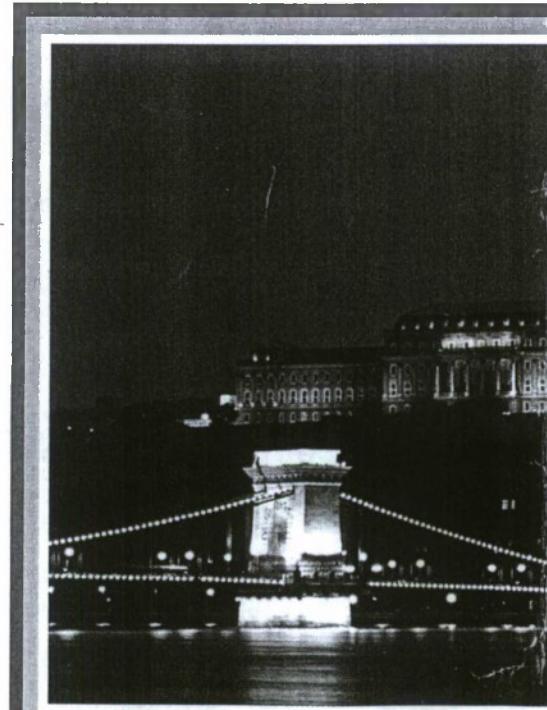
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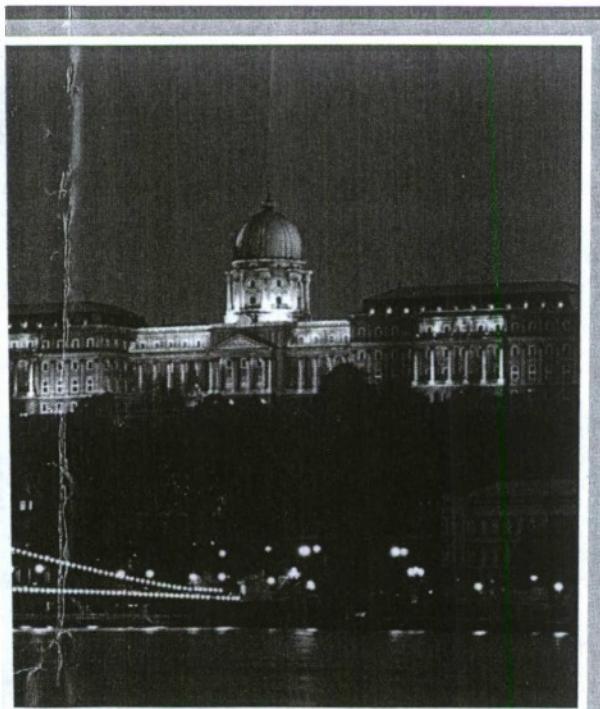
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$$\mathcal{C}_i = \sum_{u=1}^{l=i} B_{u-1}^{j=i}$$

$$\left(^u\mathbf{X}-^i\mathbf{X}\right)\sum_{u=1}^{l=i}\mathcal{C}_i+^u\mathbf{X} = ^u\mathbf{X}$$